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GEORGE REID
Editor

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VOLUME 15, No. 8 AUGUST, 1936

REFINER
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The Look Box

MOTOR vehicle taxpayers of Virginia have been saved $112,500,000 as a result of low-cost road construction program by the state highway department, according to the Western Petroleum Refiners Association. It is pointed out that this saving was made possible through construction of 5000 miles of oil and bituminous highway surfaces at a total cost of $12,500,000, in parts of the state where light traffic made expensive paving unnecessary. High-cost paving of this mileage would have cost approximately $125,000,000. Had the highway department elected to spend the same amount of money for high cost pavement, only one tenth of the highway could have been built, leaving 4500 miles of dirt roads unpaved

Roads and Road Oils

The method used in Virginia is known as "stage construction," the thickness and durability of the pavement being increased by successive applications of bituminous materials as traffic increases, producing the required road service with a maximum of economy. It is, apparently, a program well worth studying by other states, and well worth advocating by the petroleum refining industry, especially those engaged in the manufacture of road oils and asphalts.

A suggested improvement in this program, and one mentioned previously in these columns, would be the primary preparation of the road bed or base by giving it a thorough oiling or treatment with bituminous material to a depth of four to six inches and to a width two to four feet wider than the proposed road. Such preparation of the base secures a virtually "water proof" roadway and prevents infiltration of water into the base and beneath the finished road bed—and road engineers well know that it is the water infiltration and penetration which later causes most of all road bed and paving failures.

Both programs are of the type which refiners and the oil industry generally can well afford to promote—and certainly the beneficial results to be secured are such that the industry can not be accused of simply desiring to sell more road-making materials.

STATES which continue raising gasoline taxes continue to find that consumption gains are not up to the expectations of their legislators. Gasoline consumption figures of the United States Bureau of Public Roads reveal that gasoline tax increases last year resulted generally in a substantial reduction in automobile use. It is estimated that in five states where gasoline tax rates were increased last year motorists cut their mileage by more than one and one quarter billion miles.

Taxes

In these states gasoline consumption last year was only 3.7 percent above that of 1934, or about half of the 7 percent gain registered in other states. If they had enjoyed consumption gains at the rate which prevailed in the remainder of the

states an additional 100,000,000 gallons of gasoline would have been used by motorists.

All this checks back to the refinery that produces the motor fuels and to the refining companies in the business of manufacturing motor fuels as well as to those engaged in marketing gasoline—not to mention receipts of tax moneys by the states themselves. Experiences of most states taxing gasoline seems to prove that taxes running 4 to 5 and 6 cents per gallon definitely tends to lower consumption of fuel within the given state—whereas taxes of 2 and 3 cents per gallon provide more revenue for the state because of the increase in gallonage. And hence the logical concern on the part of refiners in the "Reduce the gas tax" campaign.

New Oil Reserves

SOMEWHAT more than one half of the year having passed, considerable thought is being given currently to the subject of crude oil reserves—a subject in which the refining branch of the industry has very definite interest. It has been customary to take inventory at mid-year to see if the nation has added as much new oil to the known reserves as it has taken from the ground during the half year.

During the first 6 months, about 525,000,000 barrels of crude oil was taken from wells in the United States. Meanwhile, approximately that much recoverable new oil was found in Texas alone. The nation's draught on its reserves was almost wholly compensated by the building up of new supplies that took place in Texas.

But, in addition, exploration was not by any means fruitless in other states. Outside of Texas, sizeable additions to reserves were made, and those additions represented, under the circumstances, net additions to reserves. They aggregated at least several hundred million barrels.

After several years of famine in oil discoveries, California this year has added considerably to its known reserves. Three new important fields were discovered during the first half of the year. One of them, Old River, Kern County, rates as a major field of especially promising potentialities, being probably the most important California discovery since Kettleman Hills in 1928.

This year has brought important additions to known reserves also in Oklahoma, New Mexico and Kansas, through opening of new fields, extensions of established fields, and finding new productive horizons in the existing fields. Louisiana has also furnished some new oil this year, although Rodessa's oil production and some of the other newer fields of North and South Louisiana rated originally as 1935 discoveries.

The Texas discoveries of the first half of 1936, aggregating about a half billion barrels, included new fields, extensions of older fields, and new productive sands. About half of the new oil was supplied by the eastern section of the state, largely through the discovery of the Talco field and extension of Rodessa production considerably into Texas. The Texas Gulf Coast and Southwest Texas each supplied, meanwhile, around 100,000,000 barrels of new reserves, and West Texas furnished about one half that amount.

The results in the initial half of 1936, like those of 1935, tend to support those optimistic souls who laugh at fears of a possible future shortage of oil. Those cheerful ones say that immense quantities of oil lie undiscovered beneath the numerous promising areas of the various oil producing states. At any rate, and currently, the prophets of a coming shortage of oil are without as much honor as formerly and the top place is held again by the optimists who think that the oil industry of the United States can fulfill the nation's requirements indefinitely into the future.

More About Talco Crude

THE Bureau of Mines has obtained samples of oil from two wells in the new Talco field of Titus and Franklin Counties, Texas. The analyses show the oil to be classified as wax-bearing paraffin-intermediate base oil by the Bureau of Mines method of analysis and interpretation. The sulphur content and the carbon residue of residuum are high for this classification. Considerable interest has been shown in this field because of the unusual properties of the oil and prospect for large production.

But slight difference is apparent between the crudes from two wells. King Hughes Well No. 1 is reported at 25° A.P.I. gravity with pour point of 15°F., 2.76 percent sulfur, and brownish black color. Carr Well No. 1 with 24.5° A.P.I. gravity, is reported with pour point of below 5°F., 2.77 percent sulfur and same color.

The approximate summary of products according to the present analysis reports light gasoline of 79.4° A.P.I. gravity to the extent of 3.6 percent. Total gasoline and naphtha of 63.9° A.P.I. gravity totals 13.7 percent. There is an indicated yield of 13.2 percent of 43.4° A.P.I. gravity kerosene distillate. Nonviscous lubricating distillate yield is reported as 10.3 percent, 31.1-26.3° A.P.I. gravity and medium lubricating distillate yield is 6.7 percent of 26.3°-24.3° A.P.I. gravity. No viscous lubricating distillate is reported. The residuum totals 47.0 percent with A.P.I. gravity of 10.6 degrees. Carbon residue of the residuum is 16.6 percent and carbon residue of the crude is 7.8 percent.

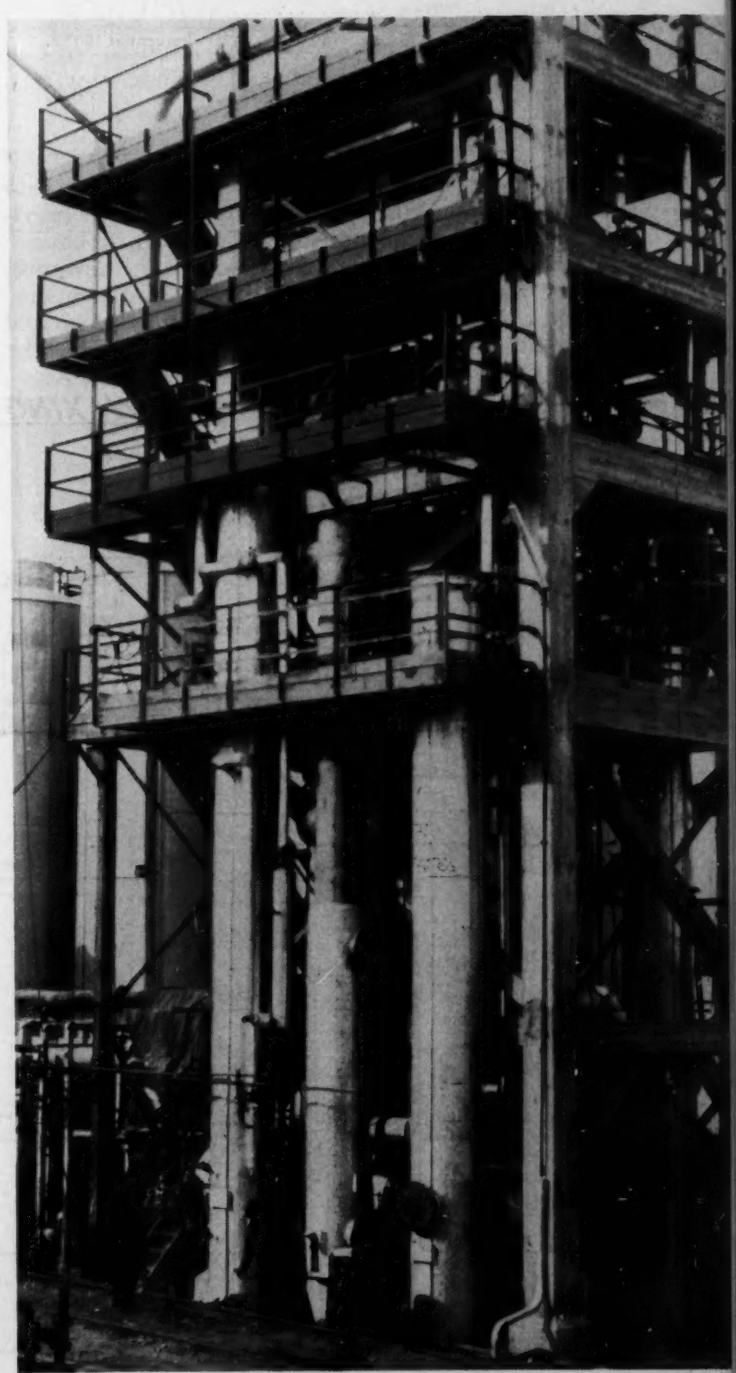
Solvent Dewaxing Process *at* Ponca City Refinery

J. C. ALBRIGHT

DUE to the fact that manufacturers of automobiles are building engines with closer clearance between moving parts, lubricating oil refiners are faced with the problem of making motor oils with lower viscosities in larger quantities than ever before. Because of this situation Continental Oil Company recently installed a solvent dewaxing unit in its Ponca City refinery to increase the available light lubricating oil base stock for blending purposes.

Refiners generally for many years have been using the orthodox methods for dewaxing in the production of low cold test lubricating oils, consisting principally of wax distillate pressing, cold settling and centrifuging. The pressing of wax distillate is limited to light distillates containing crystalline wax, while cold settling and centrifuging are limited to heavy distillates of high viscosity containing mainly amorphous wax. Due to the limitations imposed by the character of the wax, successful dewaxing by the more common methods requires close fractionation to eliminate the amorphous wax from the wax distillate, and the crystalline wax from the heavy distillate of high viscosity. Continental Oil Company installed the solvent dewaxing unit to process an intermediate cut between the wax distillate and the heavy vacuum lubricating oil distillate, or cylinder stock bottoms, manufactured in the initial distillation of the crude oil. The intermediate cut, commonly referred to as 400 distillate, contains both amorphous and crystalline waxes, which cannot be successfully removed by any of the more orthodox methods. Due to the fact that this cut can be easily dewaxed by the solvent process, pressing of the wax distillate and centrifuging of the cylinder stocks are more easily accomplished when the cut is made long enough to remove all of the amorphous wax from the wax distillate, and all of the crystalline wax from the cylinder stock bottoms, increasing the overall yield and obtaining a low cold test, wax free oil.

The stocks at Ponca City being run to the solvent



Bari-Sol Solvent Dewaxing Plant at Continental Oil Company's Ponca City, Oklahoma, Refinery

dewaxing unit have the following approximate physical characteristics:

Gravity	27.6° A.P.I.
Flash	455°F.
Fire	530°F.
Viscosity at 210°F.	57.5 Sec.
Cold test	101°F.
Wax content	11.69 percent by weight

The physical properties of the solvents used are as follows:

PROPERTIES

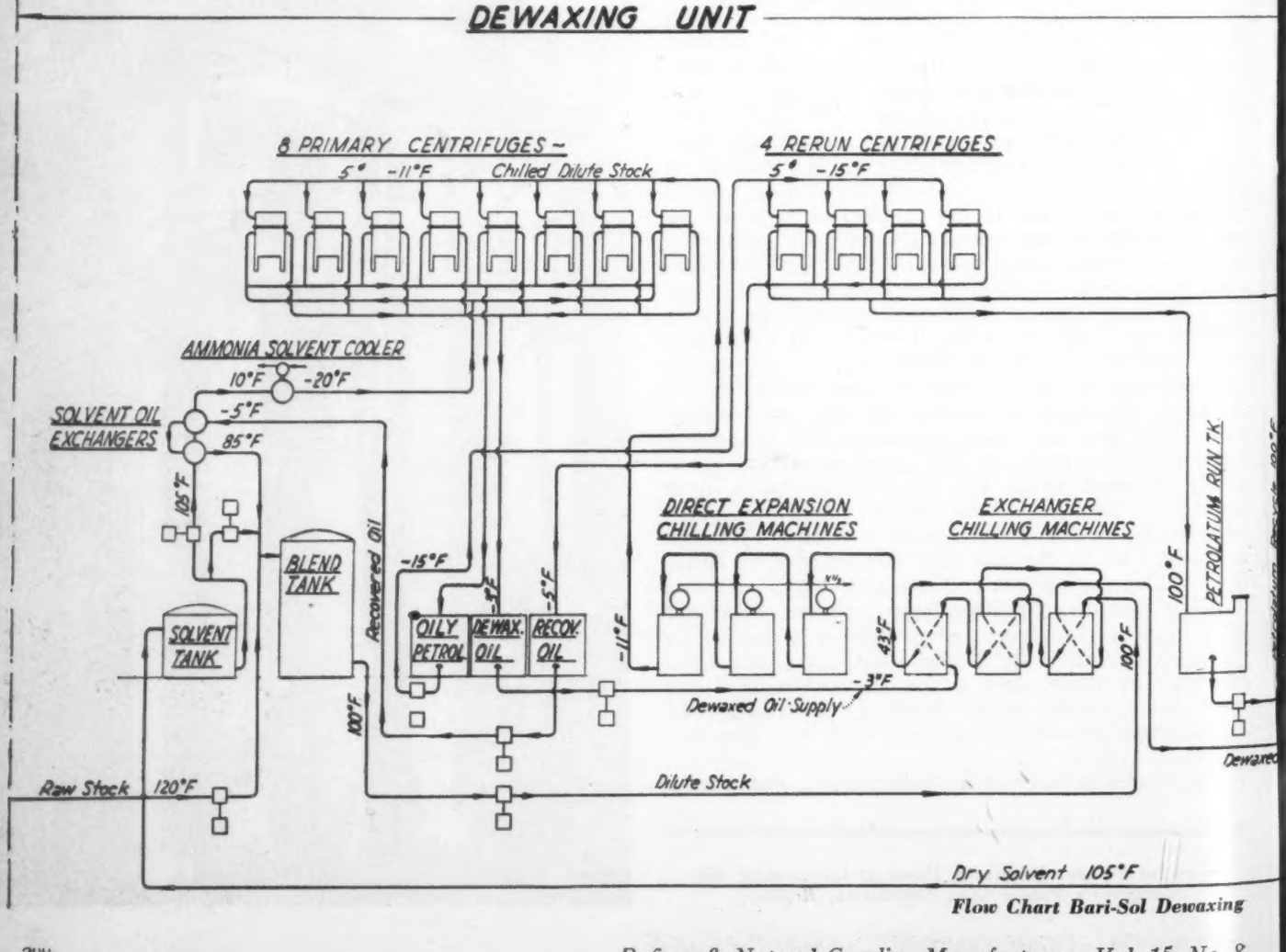
Description	Benzol	Ethylene Dichloride
Molecular weight	78.05	98.95
Specific gravity	0.805	1.257
Pounds per gallon	7.31	10.47
Melting point °C	5.5	—35.3
Melting point °F	41.9	—31.5
Boiling point °C	79.6	83.7
Boiling point °F	175.5	182.7
Chemical formula	C_6H_6	$C_2H_4Cl_2$
Solubility	**Percent at 100°F.**	
Water in solvent	0.11	.....
Solvent in water	0.16	0.90
Solvent in alcohol	100.00	Soluble
Solvent in ether	100.00	100.00

The solvent used in the process at Ponca City consists of a blend of 78 percent by volume of ethylene dichloride and 22 percent by volume of benzol. The wax precipitant, ethylene dichloride, also precipitates high viscosity index oil at low temperatures. In order that wax precipitation may be carried out to successful completion, without affecting the oil in charge, the above percentages of ethylene dichloride and benzol were found to be the proper mixture for the stocks processed.

The benzol-ethylene dichloride method is unique in its ability to dewax oil to a pour test not substantially higher than the temperature at which separation of the wax, or petrolatum, from the oil solvent takes place. This permits chilling temperatures to be used of —8°F. to —12°F. when producing a zero pour test oil, as compared with chilling temperatures of —40°F. to —45°F. necessary with the conventional centrifuge method using a solution of naphtha and oil.

The solvent plant at Ponca City consists of two separate divisions; the dewaxing unit where the waxes are separated from the oil by solvent precipitation and centrifuging, and the solvent recovery unit. The first section contains the working solvent tanks, blending tanks (for solvents and oil) run and receiver tanks, two batteries of centrifuges, the essential direct expansion ammonia chilling machines and the exchanger chillers for the recovery of refrigeration. The centrifuges were divided into two separate sections for primary and rerun operation. The first, or primary section contains eight centrifuges and the second, or rerun, section contains four centrifuges.

Four accumulators, or run tanks in the first section of the plant include one to receive the oily petrolatum from the first battery of centrifuges and another the dewaxed oil. The third receives the recovered oil from the second battery of centrifuges



Flow Chart Bari-Sol Dewaxing

while the fourth receives the petrolatum dilution before it is pumped to the section where it is stripped of the solvent. The refrigeration equipment is used to reduce the temperature of the dilute, or charging stock to that best suited for processing, by passing countercurrently through the exchanger chillers with the dewaxed oil, and through the direct ammonia expansion chilling machines.

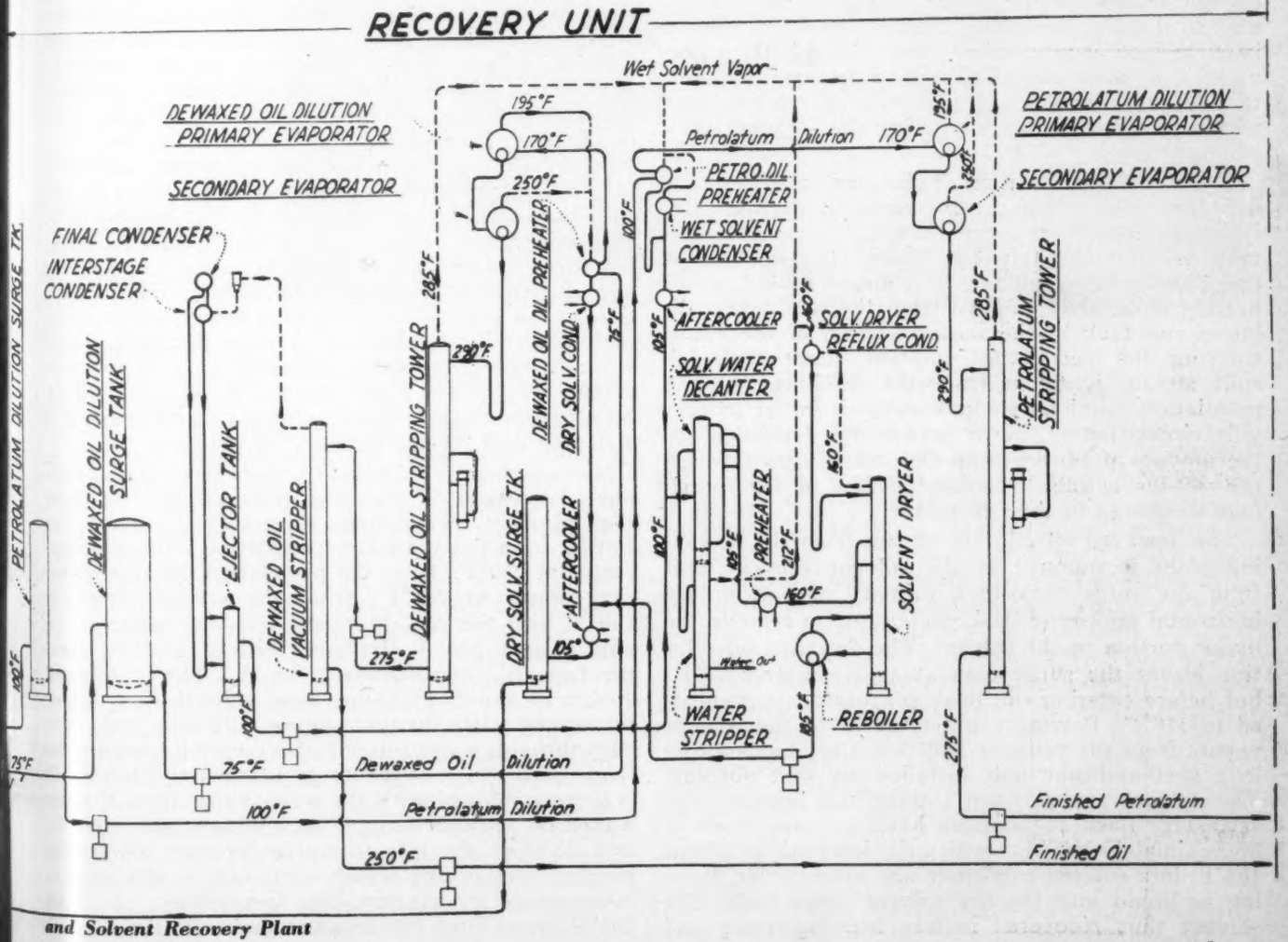
The second section of the plant contains the essential equipment for the separation of the solvents from the oils and waxes, and to purify the solvents by the removal of all moisture before they are returned to the dewaxing section for use in a continuous cycle. Two receptacles in the first part of the second section receive the dewaxed oil dilution and the petrolatum dilution, acting as supply or surge tanks before the solutions are pumped to their respective stripping columns. The columns are identical in construction, being 2 feet in diameter and 36 feet in height, equipped with 12 cast iron bubble trays, and outside reheaters connected to the side of the columns.

The raw intermediate lubricating oil cut, containing 11.69 percent of waxes by weight, is charged directly to the solvent unit untreated, having a temperature of substantially 120°F. The fresh oil stock, the solvent and the recovered oil dilution (from the secondary, or rerun centrifuges) are blended in a homogeneous mixture in a blending tank which is equipped with an agitator and steam coils, so that the temperature of the blended materials may be held at substantially 110°F. The oil containing approximately 11.69 percent wax is blended with the solvent dilution and the solvent so that the finished blend in the blend tank is in proportion of approximately three parts of solvent to one of stock, or, a ratio of 3:1.

This blended material is removed from the blending tank by pumping, directed in series, first through the exchanger chilling machines countercurrent to the cold dewaxed oil dilution, and then through the direct ammonia expansion chilling machines, where the temperature is reduced to substantially —11°F. The chilled dilute stock (raw feed, recovered oil dilution and solvent) then is charged to the 8 primary centrifuges. The amount of chilled dilute stock pumped to the centrifuges through the chilling units is governed by the pressure on the header feeding the primary centrifuges. Approximately 5 pounds is the operating pressure at this point where a pressure-control instrument actuates a pilot valve set in the steam line to the pump, which permits the pump to deliver more or less feed to the centrifuges as the header pressure indicates.

The dilute dewaxed oil representing approximately 82 percent of the original charge, discharges from the 8 primary centrifuges to the dewaxed oil accumulator, or run tank at a temperature of approximately —3°F. It is pumped continuously from this receiver to the solvent recovery dewaxed oil dilution surge tank through the exchanger chilling machines for the recovery of refrigeration, where it leaves at a temperature of approximately 75°F.

The oily petrolatum solution stream, representing



and Solvent Recovery Plant

about 18 percent of the original raw stock charge, is discharged from the primary centrifuges and flows to a run tank from which it is pumped to the four rerun, or secondary battery of centrifuges. At the end of the rundown header to the oily petrolatum solution run tank, cold solvent make-up is added in order to assist the flow of the petrolatum solution discharge and to increase the solvent-to-petrolatum solution ratio. The make-up solvent is held at approximately —20°F., so that the composite temperature of the make-up solvent, plus the petrolatum solution discharge from the primary centrifuges permits the rerunning of this dilution at approximately —15°F., or 4°F. below that at which the primary centrifuging is carried out.

The make-up solvent is chilled through two exchangers in series, countercurrent to the recovered oil to the rerun, or secondary centrifuges, and then through a direct-expansion ammonia exchanger where it leaves at approximately —20°F. There is required approximately twice as much solvent as petrolatum solution, which results in a final blend of approximately one part oily petrolatum and eight parts solvent. The run tank is equipped with a slow-speed agitator to insure a uniform blend of the oily petrolatum and the make-up solvent.

The recovered oil dilution discharge from the rerun, or secondary centrifuges, representing approximately 80 percent of the rerun charge, flows to a rerun tank at substantially —5°F. Pumped from this tank to the raw stock-solvent blending tank, it follows through the flow as described at the beginning of the process for the initial charge of oil. On the way to the blending tank, the recovered oil dilution is exchanged countercurrent with the solvent make-up of the rerun centrifuges through two shell-and-tube exchangers for the recovery of refrigeration, with a temperature upon entering the blending tank of approximately 85°F.

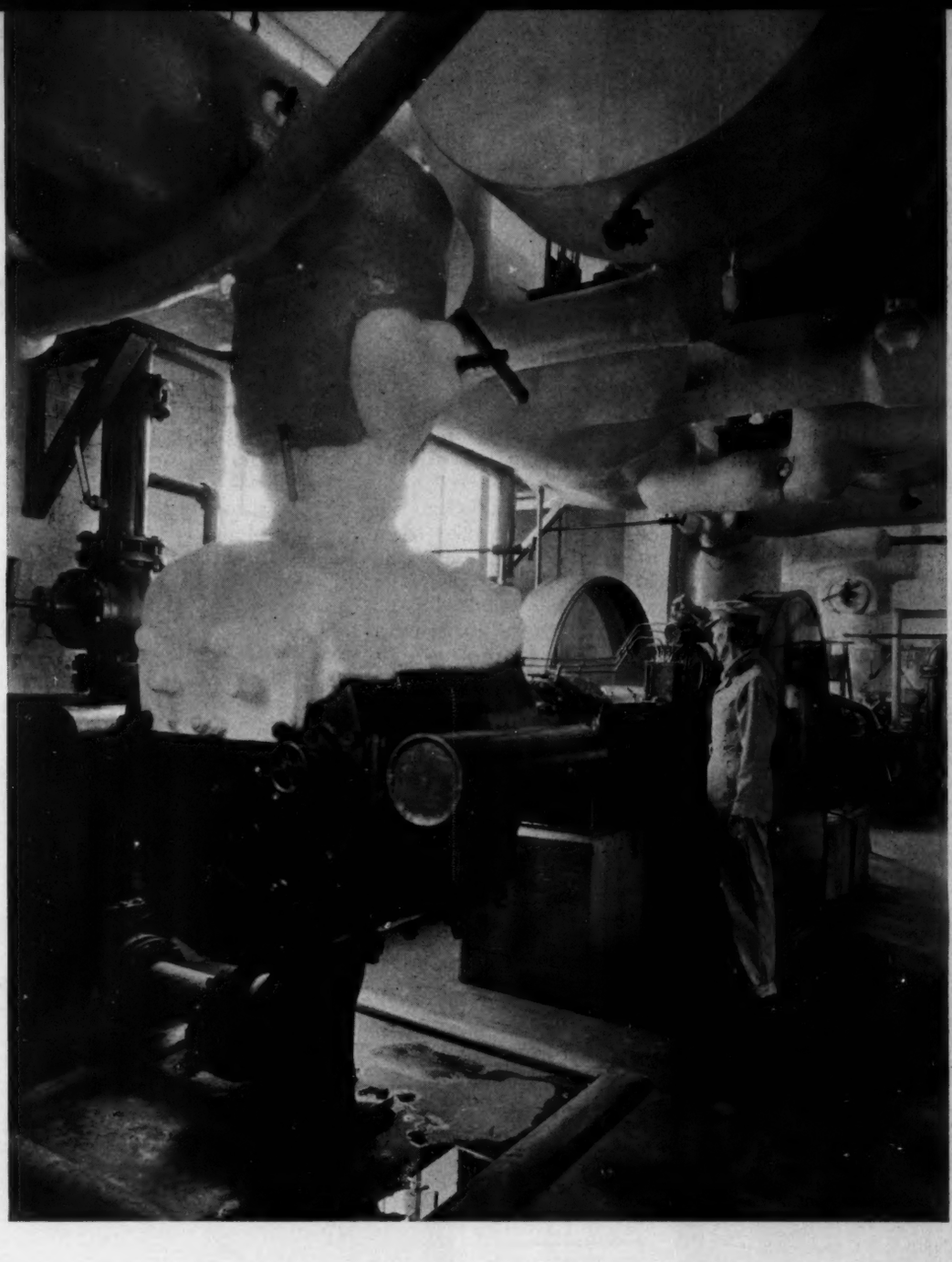
The petrolatum dilution discharge from the secondary, or rerun centrifuges representing approximately 20 percent of the rerun charge, flows into a run tank at approximately 100°F., the temperature of the dilution being obtained by means of hot water heating coils. It is pumped from the petrolatum dilution run tank to the second section of the plant, entering the petrolatum solution surge tank. A split stream is taken from the discharge of the petrolatum dilution run tank pump in order to provide circulation of warm petrolatum equivalent to the amount produced from the centrifuges through the run-down line, to assist the flow of the centrifuge discharge to the run tank.

The dewaxed oil dilution stream from the dewaxing plant is pumped to the solvent-recovery unit from the surge tank to a primary and secondary horizontal tank-type flash evaporator to remove the major portion of the solvent. The dewaxed oil dilution leaves the surge tank at approximately 75°F., but before entering the flash evaporator, is preheated to 170°F., flowing countercurrent to the solvent vapors from the primary and secondary evaporators in a shell-and-tube unit installed for that purpose. The solvent vapors upon leaving the primary and secondary flash evaporators have a temperature of approximately 250°F., which is lowered to about 105°F. in a solvent condenser and after cooler, flowing as liquid into the dry solvent surge tank. The solvent thus recovered is free from moisture and consequently does not require processing through the solvent dryer for the removal of water as is the case with all other recovered solvent streams.

The dewaxed oil leaving the secondary evaporator is delivered to the top of the atmospheric solvent stripping tower at approximately 290°F., where primary stripping is accomplished by reheating and processing with steam. The partially stripped, dewaxed oil at substantially 275°F. is pumped from the base of the primary stripping column to the vacuum stripper, operated at one half-inch Hg. absolute pressure, where the remainder of the solvent, and moisture, are removed. The vacuum stripper column is 3 feet in diameter and 18 feet in height, equipped with disengaging baffles installed below the tower feed inlet, and a mist extractor located above the feed inlet connection. Oil removed from the base of the vacuum stripper is pumped as finished oil to storage for further use in the manufacture of low cold test lubricating oil.

Substantially the same process is followed in recovering the solvent from the petrolatum dilution and the slop dilution. Slop dilution is that recovered from the drain lines of the centrifuges and process tanks and that recovered from the cleaning room. These slops are pumped to the solvent-recovery system, mixing with the petrolatum dilution before it is directed to the recovery system in this section of the unit. The solution, or dilution, is pumped from the petrolatum dilution surge tank at about 100°F. to a primary and secondary horizontal tank-type flash evaporator, similar in construction to those used in the oil dilution processing unit, for the recovery of the major portion of the solvent in the dilution. It passes through a wet solvent vapor to petrolatum dilution heat exchanger where the temperature on the petrolatum dilution is raised to about 170°F., flowing countercurrent to those vapors as they pass to the solvent-water decanter. While being partially stripped of the solvent in the two evaporators, the material is further heated until the temperature reaches approximately 290°F. Leaving the secondary evaporator, the initial pump pressure forces the partially denuded petrolatum dilution to the atmospheric stripping tower where complete separation is obtained between petrolatum and solvent. The atmospheric stripping column for separation of solvent from petrolatum is identical in construction with the atmospheric column used as a stripping unit for the dewaxed oil dilution.

The overhead wet solvent vapors from the atmospheric dewaxed oil stripping tower at 285°F., from the primary petrolatum dilution evaporator at 190°F., from the secondary petrolatum dilution evaporator at 250°F., from the petrolatum dilution stripping tower at 285°F., from the solvent drier at 160°F., and the recycle vapor from the water stripping column are all combined with a resulting temperature of approximately 183°F. The combined stream of vapors exchange heat while flowing countercurrent with the petrolatum dilution, and then pass through a condenser and after-cooler where the temperature is lowered to approximately 105°F. It is there combined with the water vapor from the dewaxed oil vacuum stripper at approximately 100°F., and flows to the solvent water decanter where the greater part of the water contained in the stream is separated by gravity. The wet solvent at about 105°F. flows from the decanter tank into the solvent



Direct expansion ammonia refrigeration system in conjunction with solvent dewaxing plant

drying tower where all of the moisture is removed by reboiling. The column used for drying the recovered solvent condensate is 2 feet in diameter by 32 feet in height, fitted with 10 cast iron bubble trays and a mist extractor at the top outlet. The dehydrated solvent is removed by pumping from the solvent drier to the dry solvent surge tank where it may be used again in the process of removing the waxes from the oil processed in the plant.

The blended solvents consisting of various percentages of benzol and ethylene dichloride require a separate step for water separation. Most of the solvent is recovered free from water through the various steps in the recovery process. The remainder of the solvent consists of overhead wet solvent vapors from the dewaxed oil and petrolatum stripping towers, from the primary and secondary evaporators and the recycle vapor from the water stripping tower. These vapors are combined and passed to the decanter where solvent saturated with water is removed and passed to the solvent drier. The water from the decanter, saturated with solvent, is discharged into the water stripper where the larger portion of the solvent is removed as an overhead vapor saturated with water which is recycled through the recovery system.

The operation of the solvent drier in the Bari-Sol process is such that water is removed from overhead, which is the higher boiling liquid, and water-free solvent is taken from the base, being the lower boiling part of the charge to this unit, differing in operation to that found in other towers in a refinery. The separation in this manner is based on Henry's law of solution, which states that the partial pressure of a component present in small amounts in a solution is proportional to its mol fraction in the sclution. Raoult's law, which is commonly used in fractionation problems, states that the partial vapor pressure of any component is equal to its vapor pressure in the pure state multiplied by its mol fraction in the solution:

Henry's Law $p=kx$
Raoult's Law $p=Px$

p=partial pressure of component from mixture.
P=Vapor pressure of pure component at the temperature of the mixture.
x=Mol fraction of component in the mixture.

The constant k in Henry's law must be an experimentally determined function of temperature, while

P in Raoult's law is fixed by the vapor pressure curve of the material. Henry's law is usually applied when the upper limit of concentration is 5 to 10 mol percent. In Engler distillations of water-saturated solvent, it has been found that unless extremely wet, an overhead cut of ± 10 percent will contain all of the water present in the original solvent. Distillation will effect separation because of the fact that, following Henry's law, the partial pressure of water in the solvent rises much more rapidly with concentration than if it followed Raoult's Law. The vapor evolved from the dilute solution of water in solvent is richer in water than the wet liquid, although the vapor pressure of the water is less than that of the solvent.

For economic reasons it has been found that the losses of solvent in the excess water removed from the system must be kept at a minimum, since the solvents used are relatively high in cost. Ethylene dichloride weighs 10.4 pounds per gallon and is sold for 5 cents per pound, or 52 cents per gallon. Ninety percent commercial benzol sells for 29 cents per gallon, making a solvent blend expense of 47 cents per gallon. It is also necessary that the water concentration in the solvent be controlled if the desirable selectivity of the solvent is maintained. It is impossible to prevent some leaks occurring in the system while operating, and provisions have been made so that dewaxed oil is furnished under pressure to the gland seal rings of the chilling machines and reciprocating and centrifugal pumps handling the solvent, dewaxed oil dilution, petrolatum dilution and other material, such as water saturated solvent and solvent saturated water, so that no losses of solvent will occur at these points.

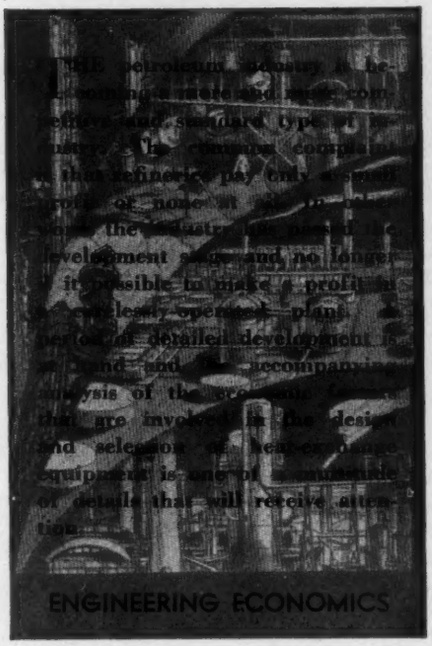
The blended solvents must be considered as being inflammable and therefore subject to explosion hazards. However, the ordinary precautions taken in refineries while handling benzine and gasoline will provide the necessary protection from explosions and fires. The explosive or inflammable range of benzol is from 1.4 to 8.0 percent, while that of ethylene dichloride is from 5.8 to 15.4 percent, by volume. The explosive or inflammable range of the solvent as a blend is between the two limits shown, depending upon the ratio of benzol to ethylene dichloride in the blend.

The greatest health hazard results from breathing high concentrations of the solvent vapors. A concentration of vapors as low as 0.1 percent is detrimental to health if inhaled for a period of eight hours. Activated charcoal breathing masks are provided and the workmen are required to wear them when any noticeable leak occurs in the plant. The solvent odor is distinct, and detectable in relatively safe concentrations, but if inhaled in concentrations which are above the low percent, it produces dizziness, vomiting and eye and throat irritations. No ill effects have been found by contact to the skin except a slight irritation.

Centrifugal wax separation plant used with solvent dewaxing process

Economics of
Heat Exchanger Design
for Handling Petroleum Oils

W. L. NELSON, ***Consultant,***
Professor of Petroleum Refining, University of Tulsa



THE two major economic factors that are involved in heat-exchange are:

(1) Money or heat is saved because heat is transferred from the hot medium to the cold charging stock, and

(2) Money is paid out for the heat-exchange equipment.

The maximum recovery of heat would be accomplished by cooling the hot medium to the temperature of the incoming cold medium. Such a practice is not feasible because a tremendously large surface is required for the transfer of heat, in fact, according to theory an infinite amount of surface would be required. If the cold medium is not heated to the temperature of the outgoing hot stock, a large number of possibilities are available and among these there will be one condition which is more economical than any of the others. These relations are indicated for a countercurrent system in Figure 1. The smaller temperature difference (to the left in Figure 1) is commonly referred to as the "approach," or in other words the outgoing temperature of one of the mediums approaches the temperature of the other medium within a certain number of degrees and this number is called the approach. In the extreme, the smaller temperature difference may approach zero as a limit and in such a case the temperature of the outgoing hot medium will be the same as the temperature of the incoming cold medium. Any larger approach is possible but inasmuch as the exchanger surface increases rapidly as the smaller temperature difference approaches zero, it is found that a certain approach, which we may designate as the economic approach, requires the least equipment cost for the recovery of a given amount of heat.

The above discussion and Figure 1 apply particularly to a countercurrent exchanger in which the quantity of hot medium is less than cold medium but the same general principles apply to other conditions such as an exchanger employing parallel flow or an exchanger in which the quantity of the heating medium exceeds the quantity of the cooling medium. Inasmuch as the above conditions of countercurrent flow and a large quantity of cooling medium are the most common ones, this pa-

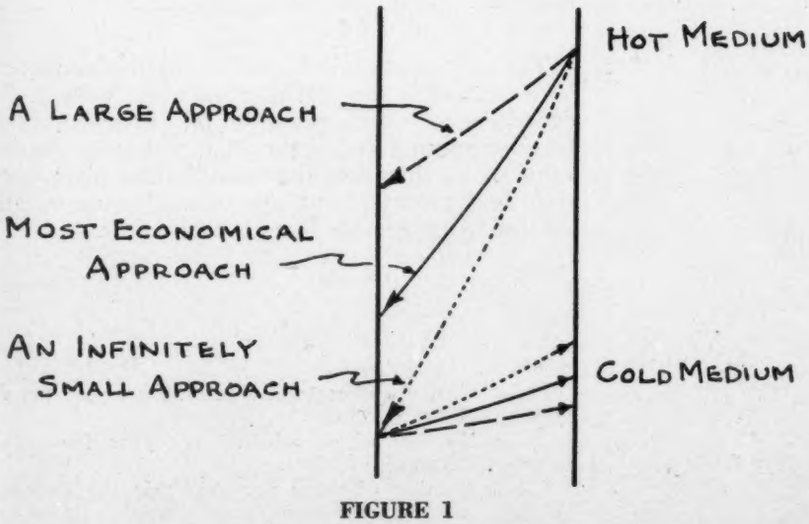


FIGURE 1

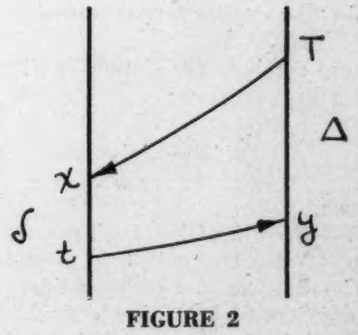


FIGURE 2

per will be limited to a discussion of this case alone.

On a basis of the dollars saved per year, when recovering one million B.t.u. per hour, the aforementioned factors may be related mathematically as follows:

$$\text{Value of heat} = 320 \times 24\, C_f$$

$$\text{First cost of equip.} = \frac{1{,}000{,}000}{dH} C_s$$

$$\text{Average interest on borrowed capitol (approx.) per year} = \left(\frac{1{,}000{,}000 C_s}{dH}\right)\left(\frac{I+0}{2}\right)$$

$$S = 320 \times 24 C_f - \left[\frac{1{,}000{,}000 C_s}{dH} + \left(\frac{1{,}000{,}000 C_s}{dH}\right)\left(\frac{I+0}{2}\right) Y\right]\frac{1}{Y} - C_e$$

or,

$$S = 7{,}700 C_f - \frac{500{,}000 C_s (2+IY)}{HY} \times \frac{1}{d} - C_e \qquad (1)$$

in which,

S = Saving, $ per year when recovering 1,000,000 B.t.u. per hour.
C_f = Value of heat, $ per million B.t.u.
C_s = Cost of surface, $ per square foot.
C_e = Cost of repairs and upkeep, $ per year per 1,000,000 B.t.u. per hour.
Y = Years to depreciate investment.
I = Interest rate divided by 100.
H = Overall transfer rate, B.t.u. per sq. ft. per hour per °F. per °F. temperature difference.
d = Logarithmic mean temperature difference.

Equation (1) can be solved for the economic approach by trial-and-error or graphical methods but it is far more convenient to state the equation as a function of the approach or smaller temperature difference so that by differentiating the equation it will be possible to solve directly for the most economical approach. The approach or smaller temperature difference is involved in two of the factors in Equation (1)—(1) the logarithmic temperature difference d, and (2) the amount of heat that is transferred.

Considering d or the logarithmic mean temperature difference—

$$d = \frac{\Delta - \delta}{\ln \frac{\Delta}{\delta}} \qquad (2)$$

in which,

Δ = the larger temperature difference.
δ = the smaller temperature difference.

These symbols are shown in Figure 2.

By a heat balance:

$$W(T-x)C = w(y-t)c = Q \qquad (3)$$

in which,

W = Weight of hot fluid, pounds.
w = Weight of cold fluid, pounds.
C = Specific heat of hot fluid.
c = Specific heat of cold fluid.
T = Inlet temperature of hot fluid.
t = Inlet temperature of cold fluid.
x = Outlet temperature of hot fluid.
y = Outlet temperature of cold fluid.
Q = B.t.u. transferred per hour.

or,

$$\frac{WC}{wc}(T-x) = (y-t)$$

$$\text{by letting, } R = \frac{WC}{wc}$$

$$RT - Rx = y - t$$

by adding and subtracting Rt and T—

$$RT - Rx + (Rt - Rt) = y - t + (T - T)$$
$$R(T-t) - R(x-t) = (T-t) - (T-y)$$

but since $(x-t) = \delta$; and $(T-y) = \Delta$,

$$R(T-t) - R\delta = (T-t) - \Delta$$
$$\Delta = (1-R)(T-t) + R\delta \qquad (4)$$

Substituting Equation (4) in Equation (2)—

$$d = \frac{(1-R)(T-t) + R\delta - \delta}{\ln \frac{(1-R)(T-t) + R\delta}{\delta}} = \frac{(1-R)(T-t-\delta)}{\ln \frac{(1-R)(T-t)+R\delta}{\delta}} \qquad (5)$$

The saving (S) involved in Equation (1) must also be expressed in terms of the approach. The heat transferred per hour is given by Equation (3) and the approach may be introduced as follows:

$$x = (t+\delta), \text{ or } y = (T-\Delta)$$
$$Q = W(T-t-\delta) \quad C = w(T-t-\Delta)c \qquad (6)$$

By letting small s designate the actual saving in dollars per year and by inserting Equation (6) in Equation (1)—

$$s = \frac{WC}{10^6}(T-t-\delta)\left[7{,}700 C_f - \frac{500{,}000 C_s (2+IY)}{HY(1-R)(T-t-\delta)}\left(\ln \frac{(1-R)(T-t)+R\delta}{\delta}\right) - C_e\right] \qquad (7)$$

This equation is a general statement of the yearly saving by heat-exchange in terms of the operating conditions and costs, and particularly the smaller approach. By differentiating s with respect to δ in Equation (7), and setting the differential form equal to zero, the following equation results:

$$\delta = \frac{(R-1)(T-t) \pm \sqrt{[R-1)(T-t)]^2 + \frac{2{,}000{,}000 RC_s(2+IY)(T-t)}{HY(7{,}700C_f - C_e)}}}{2R} \qquad (8)$$

The only constant in Equation (8) that cannot readily be estimated is the cost of repair and upkeep. This is dependent to a large extent on the particular conditions that are encountered in the plant and when possible the value of C_e should be determined from plant operating records. However, as an approximation, an equation of the following general form is suggested:

$$C_e = \frac{70a}{h} + b \qquad (9)$$

in which,

C_e = Cost of upkeep and repairs, $ per year per million B.t.u. per hour.
a = Number of shut-downs per year for repairs or cleaning of tubes.
b = Number of times per year that the exchanger is flushed with water or blown with steam.
h = Millions of B.t.u. transferred per hour.

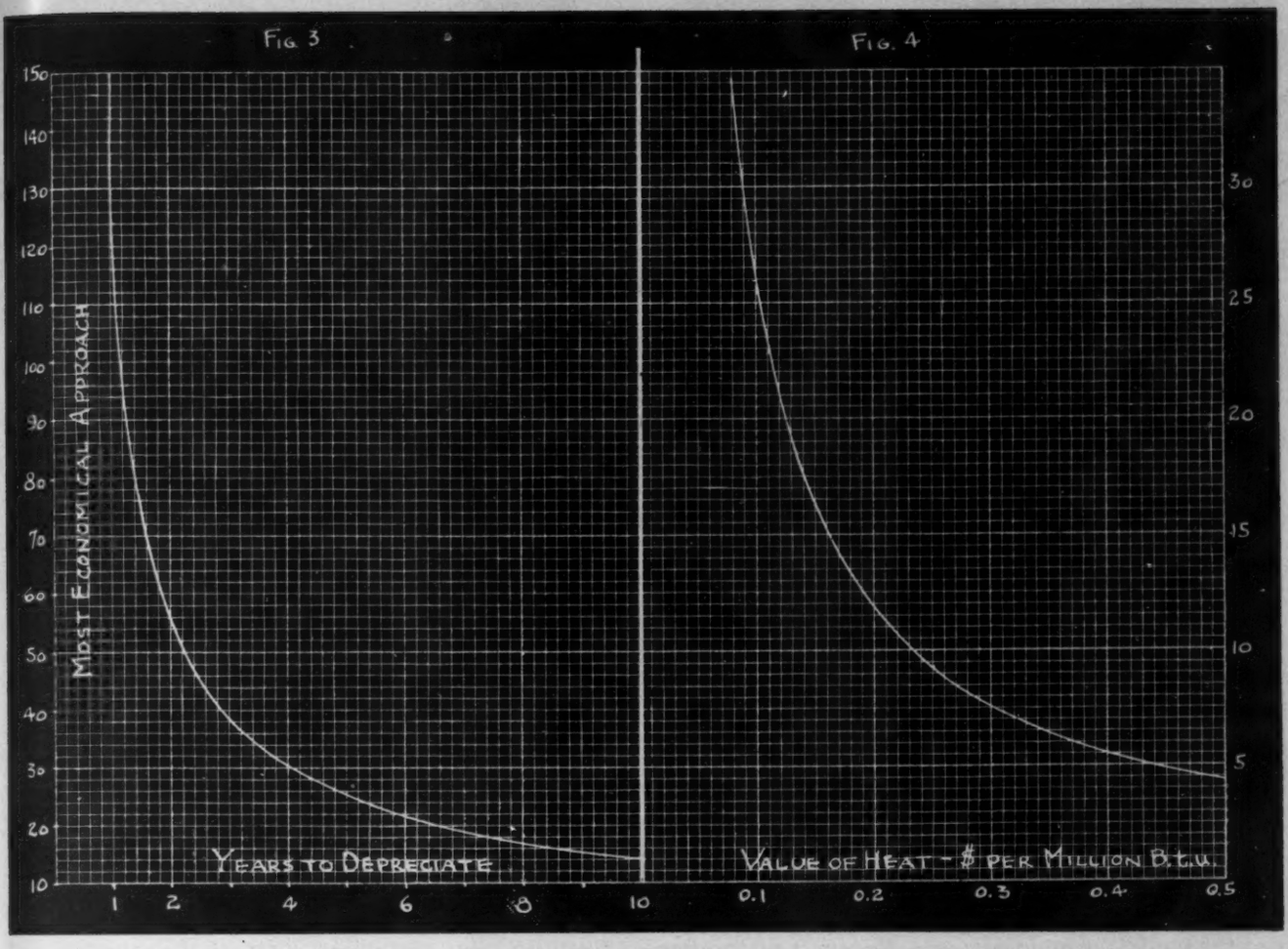


Fig. 3
Fig. 4
Most Economical Approach
Years to Depreciate
Value of Heat - $ per Million B.t.u.
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
1
2
4
6
8
10
0.1
0.2
0.3
0.4
0.5
30
25
20
15
10
5

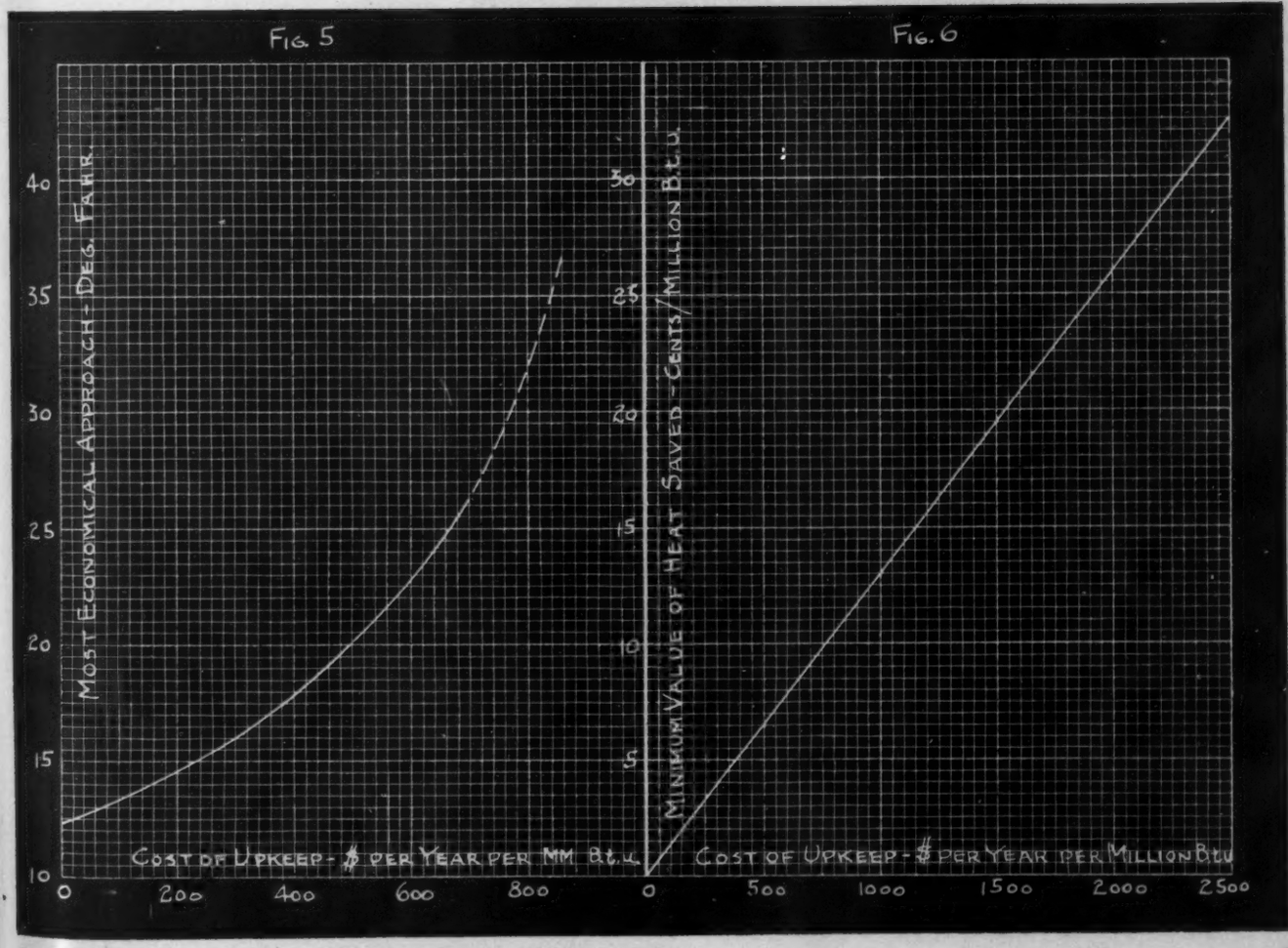


Fig. 5
Fig. 6
Most Economical Approach - Deg. Fahr.
Minimum Value of Heat Saved - Cents/Million B.t.u.
Cost of Upkeep - $ per Year per MM B.t.u.
Cost of Upkeep - $ per Year per Million B.t.u.
40
35
30
25
20
15
10
0
200
400
600
800
500
1000
1500
2000
2500
30
25
20
15
10
5

Thus for a million B.t.u. exchanger which is cleaned 4 times a year but which is not blown with steam, etc., the value of C_e is about \$280.00; or for a 2 million B.t.u. exchanger, \$140.00. If in addition the exchanger is blown with steam once a week, the value of C_e is about \$332.00 for a million B.t.u. exchanger and \$192.00 for a 2 million B.t.u. exchanger.

INFLUENCE OF FACTORS ON ECONOMIC APPROACH

The following values of the constants were estimated by a study of the average conditions in petroleum refineries:

$R = 0.16$ $\quad$ $Y = 10$
$(T-t) = 200$ $\quad$ $C_e = \$160$
$C_s = \$2.66$ (800 sq. ft.) $\quad$ $C_f = \$0.17$
$I = 0.06$ $\quad$ $H = 25$

Using these conditions, the most economical approach temperature is found to be about 14°F. This is a far smaller approach than those which have been used in many refineries and equipment companies. The only constant in those listed above that might arouse serious controversy is the 10 years for depreciating the investment. If the equipment is depreciated in a less number of years, other conditions remaining the same, the economical approach will increase as shown in Figure 3. Inasmuch as it is unreasonable to depreciate the equipment in less than 2 years, the economic approach will always be less than about 60.

The temperatures of the two fluids, the cost of surface, and the transfer rate are not important factors unless extreme conditions are encountered. The cost of surface and the transfer rate are intimately related—that is, to double the cost of the surface is equivalent to cutting the transfer rate in half, and vice versa. For the general conditions outlined above, the effect of transfer rate (or surface cost) and of the temperatures of the fluids is indicated in Table 1.

TABLE 1
Effect of H, C_s, and (T—t) on the Economical Approach

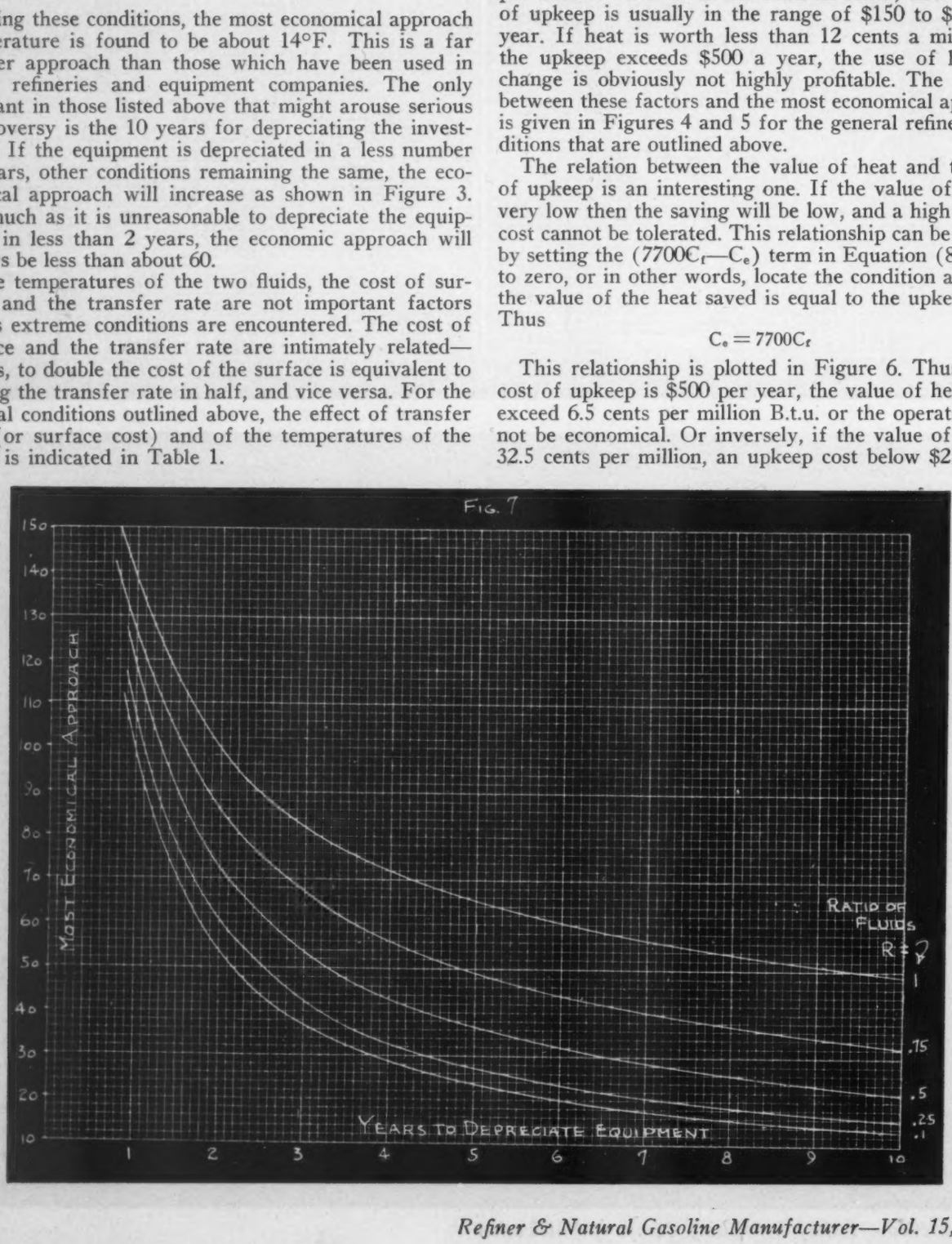
(T—t), °F.	Most Economical Approach, °F.	H, (when C_e=2.66)	Most Economical Approach, °F.	Corresponding Value of C_e, Dollars (when H=25)
100	13.9	10	33.8	6.65
200	14.1	20	17.2	3.32
300	14.2	30	11.9	1.99
400	14.23	50	6.9	1.33
500	14.27	80	4.38	0.83
600	14.29	100	3.44	0.66

The effect of the value of heat and the cost of upkeep and repair are important ones except that they usually do not vary through a great range. In other words the value of heat seldom exceeds about 25 cents per million B.t.u. or is less than 12 cents; and the cost of upkeep is usually in the range of \$150 to \$500 per year. If heat is worth less than 12 cents a million or the upkeep exceeds \$500 a year, the use of heat-exchange is obviously not highly profitable. The relation between these factors and the most economical approach is given in Figures 4 and 5 for the general refinery conditions that are outlined above.

The relation between the value of heat and the cost of upkeep is an interesting one. If the value of heat is very low then the saving will be low, and a high upkeep cost cannot be tolerated. This relationship can be studied by setting the $(7700C_f - C_e)$ term in Equation (8) equal to zero, or in other words, locate the condition at which the value of the heat saved is equal to the upkeep cost. Thus

$$C_e = 7700C_f$$

This relationship is plotted in Figure 6. Thus if the cost of upkeep is \$500 per year, the value of heat must exceed 6.5 cents per million B.t.u. or the operation will not be economical. Or inversely, if the value of heat is 32.5 cents per million, an upkeep cost below \$2500 per



year per million B.t.u. will be an economical operation. Obviously, the greater the difference between the two factors, the greater will be the saving.

In order to prepare a working chart for refinery conditions, the following factors were considered to be most important: (1) Years to depreciate the equipment, and (2) the ratio of the quantity of hot fluid to the quantity of cold fluid or R. These are related to the economic approach as indicated in Figure 7, for the general refinery conditions that have been used heretofore, but which will be repeated for clarity.

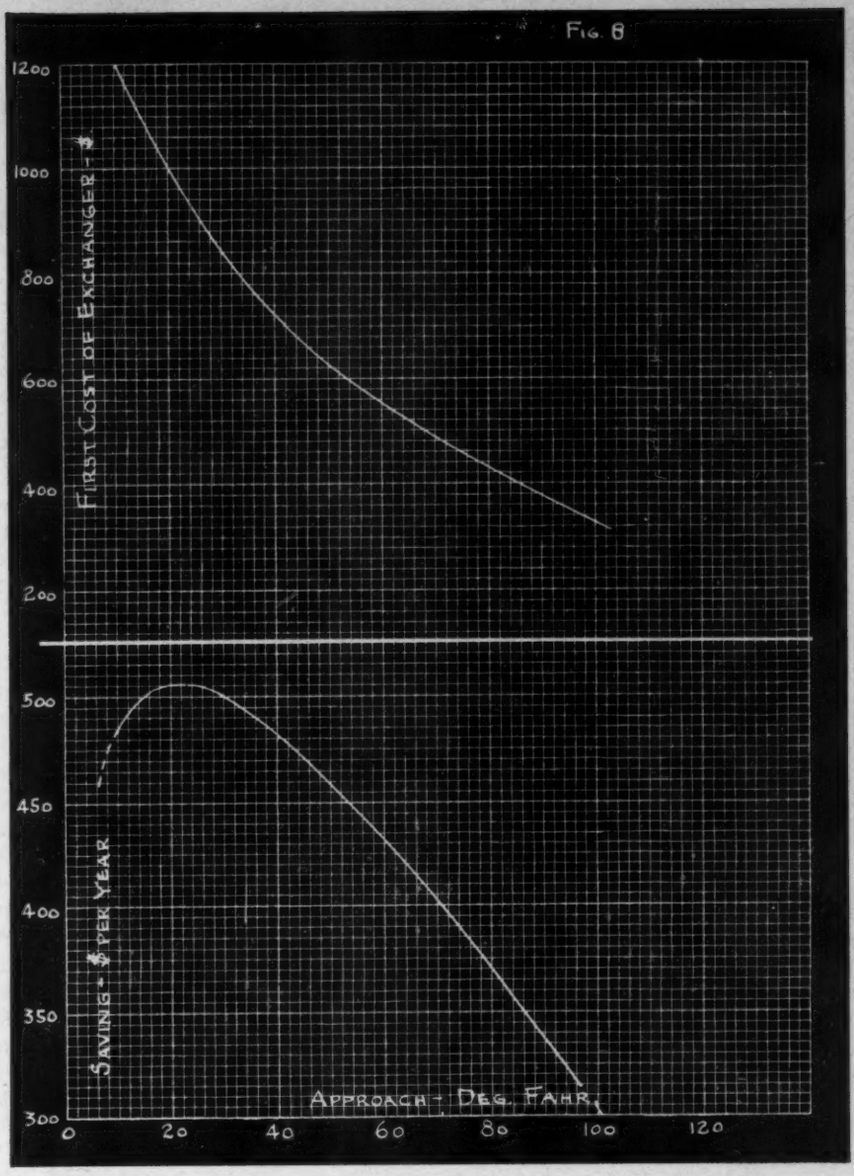
$(T-t) = 200$	$C_e = \$160$
$C_s = \$2.66$	$C_f = 0.17$
$I = 0.06$	$H = 25$

Y will be permitted to vary.
R will be permitted to vary.

Although Figure 7 is valuable as an approximation, its limitations should be kept clearly in mind, i.e., that two important factors, the value of heat and the cost of upkeep are not included. In order to take all the many variables into account it will be necessary to resort to Equation (8) or to develop a nomographic chart method of solution.

ACTUAL SAVING

The real test of the usefulness of the above formulations is the dollars saved per year by operating at the economic approach rather than at some other approach, and what additional capital investment is required in order to do so. This was investigated for a particular case by solving Equation (7) for a number of conditions and plotting the results as shown in Figure 8.



The conditions were for a kerosene-crude oil exchanger in which the kerosene was available at 420°F. and the crude oil at 240°F. The following conditions were considered as representative of such an exchanger in a 5000-barrel petroleum refinery.

$C_s = \$4$ (250 sq. ft.—1935)	$Y = 6$
$R = 0.12$	$H = 40$
$(T-t) = 180$	$C_f = 0.16$
$I = 0.06$	$C_e = 200$ (small exchanger)

An examination of the two curves in Figure 8 shows that the saving at the economic approach is about $200 per year more than the saving at an approach of 100°F. Thus in a period of 6 years the additional first cost of $650 will be repaid by operation at the economic approach and in addition a saving of $1200 will be accomplished. The heat transferred through the above exchanger was only about 700,000 B.t.u. and hence in the complete heat-exchange system of the topping unit alone, a yearly saving of about $2000 a year may be possible by providing additional surface in the existing heat-exchange system. Over an entire refinery the saving could easily reach $4000 or $5000 a year.

SUMMARY

(1) The use of a closer approach temperature between the outgoing hot medium and the incoming cold medium than the approach temperature now being used, is economically sound. In the past, the approaches that have been used ranged between 30 and 100°F., whereas it appears that approaches between 12 and 40°F. are usually justified.

(2) The factors that most greatly affect the economical approach temperature are number of years during which the investment in equipment is depreciated, the cost of upkeep and repair, and the ratio of the weights of the two fluids that are exchanging heat; although other factors such as cost of surface, transfer rate, value of heat, and the difference in temperature of the two incoming fluids, are important under certain conditions.

(3) For a given cost of repair and upkeep there is a limiting low value of heat below which it is not economical to practice heat-exchange and vice versa.

(4) The saving in a given heat exchanger does not change greatly if the approach is not exactly the economical approach and hence the use of the general curves of approach versus economic factors, such as those given in Figure 7, is sufficiently accurate for most commercial petroleum refinery conditions.

(5) The general equation (8) can be used for any countercurrent exchange system, even for other materials than oil providing the quantity of cold fluid exceeds the quantity of hot fluid.

The writer wishes to acknowledge the able assistance of Mr. Russell Claxton, a senior at the University of Tulsa, in the formulation of this material.

MODERNIZATION Economics

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THE refining industry, more than any other, has maintained its volume of business throughout the depression. This fact is strikingly shown by the figures of domestic gasoline consumption for this period. Although gasoline consumption in 1932 dropped 7.6 percent below the previous peak established in 1931, the demand since has gradually increased until an all-time record high was established in 1935. Consumption today is definitely indicating a still greater demand in 1936. Aside from being a leader in recovery, the industry has emerged in excellent financial shape. It is, therefore, in a position to take advantage of the future which promises much in the way of market conditions.

Refinery construction and replacements this year will exceed any since 1929. Plants which have been operated over the past years without needed repairs will receive attention again, and others will be rearranged or replaced in order to permit reduction in operating costs. It has been estimated that about $70,000,000 will need to be spent by refiners this year for new equipment and an additional $50,000,000 for the repair and maintenance of existing plants. The modernization of an industry which has allowed its physical equipment to deteriorate over a period of years calls for considerable engineering judgment.

Very fortunately, the depression years did not entirely eliminate engineering thought, and many developments were brought about which call for a change in refining methods. Developments in equipment and instruments have been numerous, and these can now be applied with beneficial results even in existing plants. Plants which were initially lacking in correct engineering principles are particularly susceptible to such treatment. Delays in making improvements and failure to adequately maintain existing equipment are costly. Evidence of this is furnished by the present day condition of the refining industry. The corrective measure is obviously the use of competent engineering by the management.

Two potent causes of delayed plant betterment programs are a lack of knowledge of what can actually be accomplished by proposed changes and a lack of confidence in those who support the proposed improvements. Only a very few executives are well informed about every phase of the industry with which they are connected, and fewer yet can be classed as experts. The head of any organization must therefore depend upon the services of others to accomplish the desired results, and only the poor one fails to recognize this. Such services may consist in carrying out definite instructions, or, they may require original thinking and planning.

By reason of their differences in experience, men react differently toward authorizing expenditures for improvements. In any case, their mental inertia cannot be overcome without first satisfying the two conditions; sufficient knowledge of the problems and confidence in the engineer. Thus few executives are willing to experiment with new equipment unless they are personally well informed on this particular phase of operations. For this reason it is desirable that recommendations should be made for equipment well beyond the experimental stage and upon which practical operating data is available. It follows that time is required to gather and properly present data for the enlightenment of the management. Thus the ability of the engineer to present this data, together with the solution to the problem, in a convincing manner is one of the main factors in keeping a plant up to modern economy.

The engineer must gain and keep the confidence of the management. Because of this ability, many engineers have been able to secure authorization for improvements where others have failed.

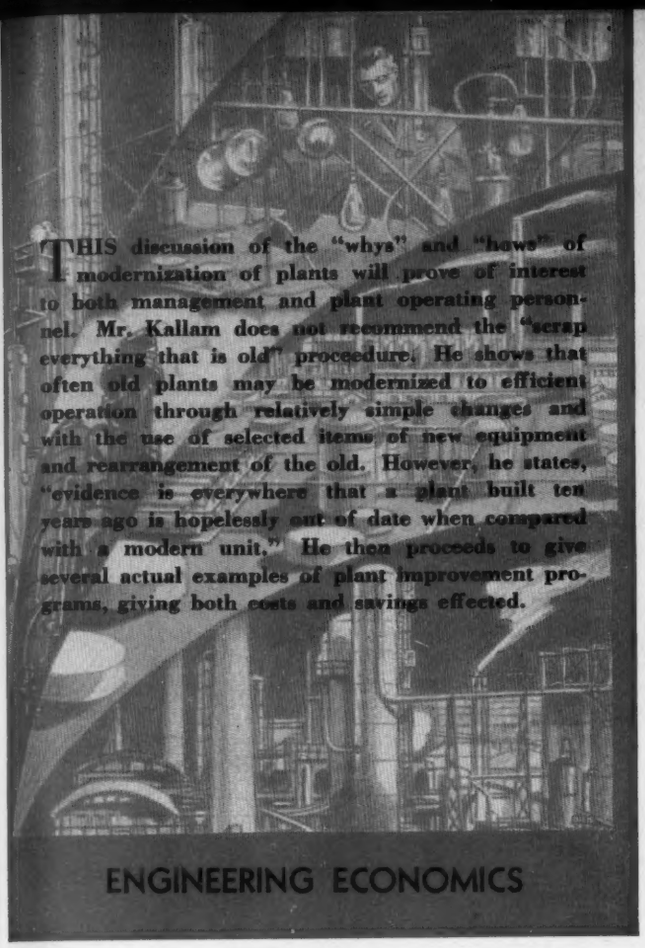
Management, whether it recognizes it or not, is continually faced with the problem of when to replace equipment. The answer is seldom clear and is generally influenced by many conditions. In simplest terms, the problem of replacing equipment can best be solved by answering the question, "Will it pay to make the change?"

Economic consideration must therefore be given such factors as increased production, reduced maintenance and labor costs, increased efficiency, improved working conditions, increased safety, and many others. Frequently, high maintenance costs are not given the weight that they should have. Too often, such costs are consolidated for the entire plant and those for the individual piece of equipment are overlooked.

Often, due either to misapplication, to radical changes in design, or to some other cause, the equipment is obsolete when first placed in service. On the other hand, certain equipment has little likelihood of becoming obsolete by reason of the service and conditions to which it is applied.

For example, motors that are properly applied may never become obsolete, but if misapplied, they may justify replacement at an early date. One common form of misapplication is overmotoring. Many motors are operated continuously at less than 50 percent of their normal rating. In the case of induction motors this is undesirable since both the efficiency and the power factor are low. It generally will pay to replace such motors with ones of proper size even though it involves sending the old equipment to the second-hand dealer.

Obviously, to maintain a refinery up to the last word in economy entails constant study of changing conditions under which it operates. It calls for the elimination of unnecessary equipment or the changing of equipment not suitable for particular conditions. In searching for possible plant losses, the common error of looking only for the large ones should not be made. Often the large ones can not be corrected because of the capital expenditures required, and the tendency is, therefore, to sit back



THIS discussion of the "whys" and "hows" of modernization of plants will prove of interest to both management and plant operating personnel. Mr. Kallam does not recommend the "scrap everything that is old" proceedure. He shows that often old plants may be modernized to efficient operation through relatively simple changes and with the use of selected items of new equipment and rearrangement of the old. However, he states, "evidence is everywhere that a plant built ten years ago is hopelessly out of date when compared with a modern unit." He then proceeds to give several actual examples of plant improvement programs, giving both costs and savings effected.

ENGINEERING ECONOMICS

and assume that nothing can be done. Trifling losses, on the other hand, should not be overlooked because they appear too small to be "not worth bothering with." Many times these simple trifling losses, when added together, amount to more than the single big loss that, because of its size, can be plainly seen. Further, the cost of eliminating the small losses may be considerably less than that for eliminating the big loss. Small losses about a plant should always be investigated.

When securities are purchased, the yield is a measure of the risk. Twenty percent is not obtainable on even gilt-edged bonds. Yet far higher percentages can often be made without risk in the refinery. In numerous cases during the past year managers took advantage of the peculiarities of their plants, along with the peculiarities of their equipment, and secured savings of considerable magnitude on the investments in modernization. Several of these instances will be cited to illustrate the savings possible through keeping plant operations up-to-date.

Consider first the case of a compressor plant where the engine jacket water was supplied by a centrifugal pump direct connected to a 100 horsepower motor. This pump was a single-stage design and rated for 1500 gallons per minute at 1450 revolutions per minute, against a 64.5-pound head. As the required pumping head was low, the pump was found operating with a throttled discharge to give only the necessary 35-pound pressure.

By reducing the impeller diameter of this pump it would have been possible to effect this desired lower discharge head, but only at the expense of decreasing the operating efficiency. Little saving would therefore result over the original method of operation. As a result, it was decided to install an entirely new pumping unit, or one which would more nearly meet the specific requirements of the service. This unit was powered with a 30 horsepower, 1450 revolutions per minute motor, direct connected to a pump having a capacity of 1200 gallons per minute against a 34.4-pound head.

Actually, the installation cost of this new pumping unit, including all labor and material, was $700. The saving in electric power over the previous operation was found to average $115 per month. Thus the capital investment of $700 was recovered within a period of approximately six months, and since which time the unit has produced a saving in reduced electrical consumption of $115 per month when compared with the original installation.

An example of savings made through modernization is that of a gasoline plant utilizing pumping equipment over 10 years old. These pumps were of the centrifugal type direct-driven by constant-speed electric motors. As is usually the case, the major part of the electrical power consumption was concentrated in the services of pumping oil, water and reflux. Naturally, it was toward these units that attention was directed when economy of operation was considered.

The design of centrifugal pumps during the past few years has so greatly improved the performance of this type of equipment that the use of the original units was obviously uneconomical. Further, because of the all-electrical drive employed in this plant, live steam was used for stripping purposes in the still. It was likewise obvious that this practice was uneconomical. After a careful study of the various ways and means to correct these conditions, the following program of changes was chosen and carried out:

New, high-efficiency pumps were purchased for circulating the lean oil, fat oil, and reflux, in each case retaining a corresponding unit of the old equipment for standby service. A new cooling-water circulating unit was also purchased, but in this case, the pump was driven from a steam turbine rather than an electric motor. The turbine was selected to operate at a back-pressure of 35 pounds, which permitted the exhaust steam to be utilized in the still in place of live steam. One of the original motor-driven water pumps was retained as a standby unit. This unit is, of course, only operated when it becomes necessary to repair the main water pump, at which time live steam is again used in the still.

The capital cost required to purchase the new equipment and completely install it in the plant was approximately $5500, exclusive of engineering fees. In so doing, the monthly saving in the cost of electric power and steam over the previous operation was $600. Thus the management received its initial expenditure back in nine months, and at the same time, effected a very considerable saving in power cost. A reduction in this item means a lower cost to produce a gallon of finished gasoline.

A compressor booster plant furnishes yet another illustration of what can be accomplished in the way of reducing operating costs. This particular plant had operated over a period of eight years. The greater part of this period was in profitable times, when high maintenance of the various units forming the station passed unnoticed. As is so often the case when business is good, profit resulted despite the inefficient methods employed. With decreasing gas supply in this plant, however, the profits became a deficit, and the management became aroused to determine the cause.

By checking what records existed for the life of

the plant, and investigating the existing operating conditions, it was obvious that the jacket-cooling-water facilities were inadequate. This fact, coupled with faulty piping arrangement, very readily accounted for the great number of power cylinders which had to be replaced because of breakage. By rearranging the cooling tower and water coolers, and entirely repiping the water system to the engine cylinders, the upkeep cost on this plant was largely reduced.

The expenditure required to recondition the cooling system was $5500. This resulted in reducing the plant upkeep. These savings made in direct engine upkeep returned the capital investment in 14 months, and with the resulting lower maintenance expense, the plant again showed a profitable operation.

Another case of interest, and one which is commonplace, was a plant where a very high oil rate was necessary in order to bring about the desired extraction of the natural gasoline from the gas. It was pointed out that a new absorber of modern design would be desirable despite the fact that the plant extraction could not be improved. In other words, while no increase in gasoline would result, the same extraction could be accomplished with 45 percent less oil rate. Obviously, the circulation of 45 percent less oil reduced the heating load on the preheater and still, reduced the cooling water required, and reduced the steam needed by the pumps. As the boiler plant was of very nominal capacity, the reduction in steam requirements was particularly beneficial from the standpoint of boiler maintenance. A further saving resulted in the revenue obtained from the gas company for the additional dry gas made available for sale purposes.

In place of installing an entirely new absorber, one of the existing shells was equipped with modern designed plates. Thus a total of $5956 was expended in this plant in order to reduce the oil circulation 45 percent. This first cost was returned within a period of five months from the savings made in boiler upkeep and increased revenue from dry gas sales.

Although much has been written on the economics of replacements, attempts to apply the various formulas and analyses to actual plant conditions has afforded management little satisfaction. Many equipment manufacturers also offer aid in analyzing managements' problems. As such service is usually gratis, the selections should be carefully scrutinized to see if they are entirely free from bias and do not reflect the ultimate desire to consummate an equipment sale. It is not surprising, therefore, that the average executive approaches the problem of plant modernization in a state of bewilderment. Nevertheless, he should avoid certain common errors in the solution of his particular problem.

Perhaps one of the most serious errors in comparing equipment is the failure to make the comparisons on similar duty. Too often it is assumed that the different outputs or capacities of two pieces of equipment can be utilized. Comparison should always be made upon the basis of the production required, and that production must be identical for the two alternative methods under consideration.

Another common error is the assumption that certain expenses will be the same under both conditions considered. Seldom is this the case. Labor will vary, material costs differ, and in most cases, overhead will vary. Obviously, every item of expense in connection with the two methods must be considered in detail to determine the effect of the new equipment or operation.

Basically, the substitution of a new piece of equipment for an existing one, or a new flow arrangement for an old one, will depend upon the relation of the resulting savings to the added investment required. If the savings represent an adequate return on the added investment, then the change should be made. New equipment or processes should not be burdened with earning a return on past mistakes. Thus when old equipment can be used for partial payment on the new, either through sale or exchange, it should so be utilized. In such cases the amount of capital investment necessary to accomplish the desired savings is correspondingly reduced and the replacement becomes far more attractive.

When considering reduction in operating costs, the tendency is to turn to new equipment and rebuilding of the old, and yet regardless of the program adopted, one item which is most consicuous in any method is the human element. Consideration should always be given the man who is to run the plant day in and day out. Remember his physical and intellectual limitations. Make the process pleasant and easy to operate. A plant that is designed with an intelligent consideration of its operating personnel is a stimulant to high efficiency, while one that is not may literally be a nightmare to both the operators and the management.

Every worker expects pay for his work and will do a sufficient amount to hold his job, but few take more than a passing interest in what they are doing. There is some question if they are altogether responsible for such lack of interest. The average employee may usually be content to sit back and let someone else do his thinking for him, being satisfied to keep running the process entrusted to him. The real operator, the type classified as excellent, looks farther. He realizes that, being in close touch with the actual operation and manufacture, he is in the best possible position to suggest changes and improvements. Is he encouraged in this? Poor performance from a plant is often not so much a criticism of the operating staff as it is of the management which permits or compels the operation of equipment that is unprofitable, obsolete, and possibly unsafe.

Evidence is everywhere that a plant built ten years ago is hopelessly out of date when compared with a modern unit. The chances are even good that such a plant is actually a liability. This does not necessarily mean that the equipment in those older plants is obsolete. A plant may be out of date and inefficient while most of the equipment in it may be in excellent condition, requiring only a rearrangement and perhaps the addition of a new key piece of apparatus. A new absorber, a still, or even a pump may be all that is required to fully modernize a plant and bring the operating efficiency into line with modern practice.

By studying advances made in refining technique during recent years the purpose is not to prove that your plant is worthless, but rather to raise the question, "Can my plant do better than it is doing?" A consideration of possible changes in arrangement and equipment of the plant from the standpoint of the savings justifying the new investments is well worthwhile. Such a course of investigation will lead to the day when you can take a visitor and say with pride—"This is the best plant possible for our particular conditions."

A New High Octane Blending Agent

H. E. BUC and
E. E. ALDRIN*

PETROLEUM chemists the world over have for many years been seeking new materials suitable as high anti-knock fuels by themselves or as blending agents in the preparation of base stocks to which some anti-knock compound such as tetraethyl lead could be added in small quantities to give the desired high anti-knock value. Technical iso-octane is one such material already made commercially available. The petroleum industry has now succeeded in providing a new material to supplement technical iso-octane. This material is isopropyl ether. Contrary to the behavior of ethyl ether which is a violent knock inducer, isopropyl ether along with some other ethers has been found to be an exceptionally good anti-knock fuel. During the past eight years experimentation has progressed on this material and methods of manufacture studied until at this time it appears to be an important factor in the successful solution of the high anti-knock fuel problem. Full scale multi-cylinder engine tests, mentioned later, have demonstrated its remarkable anti-knock qualities and in physical characteristics it apparently meets the requirements of present day military and commercial aviation fuel specifications when blended with aviation gasoline in proportions to give 100 octane with 3 cc. of lead tetraethyl.

PHYSICAL CHARACTERISTICS

The physical characteristics of isopropyl ether are shown in Table 1, along with corresponding values for pure iso-octane and benzene shown for comparison. Although a low-boiling material, its vapor pressure is below the maximum allowed for aviation gasolines and when blended therewith, vapor pressures will be entirely suitable. Freezing point is low and thus it does not have this disadvantage of the benzene or benzol blend fuels. Latent heat of vaporization, while lower than for benzene, is comparable with that for iso-octane and consequently the same maximum engine horsepower would be anticipated from considerations of mixture cooling effect, and no increase in tendency to cause carburetor icing due to excess refrigerating effect would be anticipated. Heating value on both a weight and volume basis is lower than for either iso-octane or benzene and this normally would be expected to give a reduction in miles per gallon or conversely would require greater tank capacity for a given cruising radius. The magnitude of this disadvantage is in proportion to the quantity of isopropyl ether used in the final blend and, as will be shown later, may be wiped out in practical blends by permitting of leaner air-fuel ratios without excessive head temperatures.

In considering the physical characteristics of aviation gasolines, the subject of water tolerance is of major importance. The existing specifications for water tolerance of aviation fuels require only that, when 80 ml. of the fuel are shaken with 20 ml. of water at room temperature, the increase in volume of the water layer shall not exceed 2 ml. This requirement is directed against the use of alcohol blends from which the alcohol is usually easily separated by the addition of water. Isopropyl ether has only very slight solubility in water and the above water-tolerance test usually shows no measurable increase in the water layer, even when concentrations of 40 percent are used in blends with aviation gasoline.

The low solubility of isopropyl ether in water was demonstrated by a more accurate analysis than the above rough test. Five hundred three ml. of a 40 per-

*A Digest of a paper presented before the Society of Automotive Engineers, White Sulphur Springs, June, 1936.

TABLE I

Physical Characteristics of Pure Compounds

	Isopropyl Ether	Pure Iso-Octane	Benzene
Boiling Point, °F. at 760 m.m. of Hg. Pressure	154 (153-158)	211	175
Density at 68°F. (20°C/4°C)	0.725	0.691	0.878
Refractive Index at 68°F	1.3680	1.3921	1.5014
Freezing Point, °F	—125	—162	42
Viscosity, Centipoise at 68°F	0.322 (68°F.)	0.543 (65°F.)	0.647 (68°F.)
Latent Heat of Vaporization, B.t.u./lb.	123	130	170
High Value of Heat of Combustion, B.t.u./lb.	16,900	20,580	17,650
Low Value of Heat of Combustion, B.t.u./lb.	15,600	19,200	17,000
Low Value of Heat of Combustion plus Latent Heat of Vaporization, B.t.u./gallon	95,100	111,400	125,700
Reid Vapor Pressure, lbs./sq. in. at 100° F.†	5.3	2.2	3.2

†Reid Vapor Pressure determined on commercial products rather than C. P. compounds. In case of Benzene, vapor pressure value is for commercial 90% Benzol. Particular emphasis should be placed on the freezing point of Iso-propyl Ether. Freezing which has occurred with Benzol in practice may have been due to Benzol itself. Some freezing has occurred at very high altitudes and low temperatures in exposed fuel systems from water obtained in ordinary gasoline. Also, attention is called to the Latent Heat of Vaporization for Iso-propyl Ether being even better than gasoline from the carburetor refrigeration standpoint.

TABLE II

Storage Tests on Aviation Gasoline in Hot Room at 100°F.

Blend:—60% Aviation Gasoline—40% Iso-propyl Ether—Unleaded and with 3 cc. Lead/gal., and with 1.4 mg. B.A.P. inhibitor per 100 ml.

Blend	50 Gallons Unleaded				50 Gallons Leaded				5 Gallons Unleaded				5 Gallons Leaded			
Storage Container	New Galvanized Drum		Used Galvanized Drum		New Galvanized Drum		Used Galvanized Drum		Tin Can		Tin Can+ 1 Qt. Sea Water		Tin Can		Tin Can+ 1 Qt. Sea Water	
Date of Sample start—1/30/36	1/30	4/13	1/30	4/13	1/30	4/13	1/30	4/13	1/30	4/13	1/30	4/13	1/30	4/13	1/30	4/13
Cu Dish Gum (mg/100 cc)	4.5	4.0	4.5	3.0	4.5	4.0	4.5	3.0	3.5	2.5	3.5	3.5	3.5	4.5	3.5	4.0
Army Gum (mg/100 cc)	1	2	1	2	1	2	1	Trace	1	1	1	Trace	1	Trace	1	1
Air Jet Gum (mg/100 cc)	1	1	1	1	1	1	1	Trace	1	Trace	1	Trace	1	1	1	1
Oxidation Induction Period in Hours*	7.9	9.7	7.9	10.0	10.5	9.4	10.5	15.3	7.9	14.6	7.9	7.3	10.5	6.9	10.5	7.8

*20 ml. of sample at 212°F. under oxygen pressure of 100 lbs./sq. in.

cent blend of isopropyl ether in aviation gasoline were shaken with 497 ml. of water until equilibrium was established. The final contraction of the gasoline layer was 2.63 ml. or 0.52 percent. The water content of the gasoline layer was then determined (by a method described below) as 0.09 percent. Since no change was found in the total volume (1000 ml.) of gasoline and water the total loss of isopropyl ether by solution in water was 0.61 percent on the basis of the original blend or 1.5 percent of the isopropyl ether itself.

The above results indicate the magnitude of the loss of fuel that might possibly be suffered if a blend of isopropyl ether were stored over water for long periods. This possibility has practical significance in view of the occasional use, for example in the United States Army Air Corps, of water displacement storage systems.

However, another aspect of the problem of water tolerance, which is sometimes of importance, is the tendency for aviation gasoline to dissolve water which may later be deposited at freezing temperatures as ice in the fuel feed systems of airplanes in flight. This difficulty has occasionally been encountered in the past with aromatic blends.

In this connection, the most practical consideration is not the amount of water dissolved in the gasoline at any given temperature but rather the amount of water that drops out of solution as ice at any given temperature below the freezing point of water. Accordingly, in comparing the water tolerance of isopropyl ether with that of other types of aviation fuel, two different methods of determination were used. In one set of tests, the total water content of the fuel, when saturated with water at 77° F. or at 32° F. was determined. In these tests, calcium hydride was added to the water saturated fuels and the hydrogen evolved by reaction with the water was accurately measured in a gas burette and calculated back to its equivalent in milliliters of water per 100 milliliters of fuel. The water contents of three types of fuel were as follows:

	Ml. of Water/100 ml. Saturated at 77°F.	Ml. of Water/100 ml. Saturated at 32°F.
100% Regular Aviation Gasoline	0.007	0.006
Aviation Gasoline with 40% Benzol	0.022	0.019
Aviation Gasoline with 40% Isopropyl Ether	0.085	0.062

In the second series of tests, in which the actual water separation was measured, it was shown that although the isopropyl ether blends dissolve more water at 77° F., they also retain more water in solution at temperatures as low as —20° F. Consequently, the tendency to separate is not as great as appears from the water content at 77° F.

In the second series of tests, the ice separation at —20° F. was determined directly. The aviation fuels were saturated with water at 70° F. and then pumped first through a precooler at 32° F. and thence into an ice trap at —20° F. At the end of each test, the ice trap was disconnected and its water contents were distilled with air through a weighed drying tube. The weight of water was then obtained directly. The results on the same fuels as used in the previous tests were as follows:

	Ml. of Water Separated at —20°F. per 100 ml. of fuel Saturated at 77°F.
100% Regular Aviation Gasoline	0.0005
Aviation Gasoline with 40% Benzol	0.0030
Aviation Gasoline with 40% Isopropyl Ether (2 Tests)	0.0050 and 0.0060

The above results show that the blend of isopropyl ether deposited hardly twice as much water as the benzol blend and ten times as much as the regular aviation gasoline. Furthermore, in two more tests at —10° F. on the blend, in one of which the fuel contained an additional 0.5 percent of methanol, it was found that, although the same volume of separation occurred in both cases (0.0050 percent) the separation occurred as ice in the absence of methanol and as liquid in the presence of methanol. The melting point of the ice was +25° F. and the freezing point of the liquid, which was found to contain about 40 percent methanol, was —50° F. It appears, therefore, that the tendency for isopropyl ether to take up water, although meriting attention under some conditions, is not an important handicap to its use in aviation fuels.

Another characteristic of major practical importance in determining the acceptability of a fuel is its storage stability. Blends of isopropyl ether in aviation gasoline have low gum content by all the usual methods of test. With the addition of 1 to 2 milligrams of gasoline inhibitor per 100 ml., these blends also have satisfactory resistance to oxidation. The induction period determined at 212° F. under oxygen pressure of 100 pounds per square inch exceeds 7 hours. The best motor gasolines rarely have an induction period exceeding 6 hours.

The gum tests and the oxidation test are usually accepted as measures of the storage stability of a fuel. However, actual storage tests are also being made to confirm the indications of the accelerated tests. Table 2 shows the preliminary results of stor-

TABLE III
Characteristics of 100 Octane Aircraft Engine Fuels

	Requirements for Grade 100*	U. S. Navy Requirements	British Air Ministry Requirements	Pratt and Whitney	Wright Aero.	New 100 Octane Fuel (40% Isopropyl Ether in Aviation Gasoline)	100 Octane Fuel (45% Iso-Octane In Aviation Gasoline)	Typical Aviation Gasoline	Typical Inspection Commercial 100 Octane Aviation Gasoline
Octane Number, Army Method	100	.....	.....	.....	.....	100	100	74 (ASTM)	100
Ml. Tetraethyl Lead per U. S. Gallon	3 max.	3.27 max.	3.33 max.	.....	.....	3	3	.....	3
Copper Dish Corrosion Test	Must pass	Must pass	.....	Must pass	Must pass	Passes	Passes	Passes	Passes
Gum after Accelerated Ageing Test, mgs./100 ml.	10 max.	10 max.	20 max.	10 max.	10 max.	9.8	5.0	2.0	2.0
Sulfur percent	0.10 max.	0.10 max.	0.15 max.	0.10 max.	0.10 max.	0.02	0.02	0.026	0.02
Distillation Test:									
Percent Condensed at 150°F	.....	.....	.....	5 min.	.....	8.5	5.0	9.0	9.0
Percent Condensed at 158°F	.....	.....	.....	10 min.	.....	22.0	8.0	19.0	15.0
Percent Evaporated at 167°F	10 min.	.....	10 min.	.....	10 min.	47.5	14.0	32.0	21.5
Percent Condensed at 167°F	.....	10 min.	.....	.....	.....	.....	.....	.....	.....
Percent Evaporated at 212°F	50 min.	.....	50 min.	.....	50 min.	90.0	64.0	83.5	68.0
Percent Condensed at 212°F	.....	50 min.	.....	.....	.....	.....	.....	82.5	.....
Percent Evaporated at 275°F	90 min.	.....	.....	.....	90 min.	99.0	.....	.....	.....
Percent Condensed at 275°F	.....	90 min.	.....	.....	.....	.....	.....	98.0	.....
Percent Evaporated at 302°F	.....	.....	90 min.	.....	.....	.....	.....	.....	.....
Sum of 10 and 50% Evap. Points °F	307 min.	.....	.....	.....	.....	319	364	333	354
Percent Residue	2 max.	2 max.	2 max.	2 max.	2 max.	1.0	1.0	1.0	1.0
Reid Vapor Pressure lbs./sq. in.	7 max.	7 max.	7 max.	7 max.	7 max.	6.0	6.0	6.6	6.7
Freezing Point, °F	—76 max.	—76 max.	—76 max.	—76 max.	—76 max.	below—148	below—148	below—76	below—76
Water Tolerance: (ml. Change in Volume of 20 ml. Aqueous Layer after Shaking with 80 ml. Gasoline at 75°F.)	2 max.	.....	.....	.....	.....	.....	.....	.....	.....
Product of High Value of Heat of Combustion (B.t.u./lb.) by Specific Gravity	13,700	.....	.....	.....	.....	14,310	14,350	14,400	.....
Gravity °A.P.I.	.....	.....	.....	.....	.....	64	70	70.0	70.8
High Heat of Combustion B.t.u./lb.	.....	.....	.....	.....	.....	19,360	20,820	21,000	.....
Low Heat of Combustion B.t.u./lb.	.....	.....	.....	.....	.....	17,990	19,410	19,580	.....
Low Heat of Combustion plus Latent Heat of Vaporization:									
B.t.u./lb.	.....	.....	.....	.....	.....	18,120	19,550	19,720	.....
B.t.u./Gallon	.....	.....	.....	.....	.....	109,400	114,500	115,100	.....
Percentage loss in Calorific Value as compared with Typical Aviation Gasoline:									
On Pound Basis	.....	.....	.....	.....	.....	8.1	0.9	.....	.....
On Gallon Basis	.....	.....	.....	.....	.....	5.0	0.5	.....	.....

*Compare U. S. Army Specification No. 2-92 for Aircraft Engine Fuel, Grade 100.

age tests now in progress. After 2½ months at 100° F., the stability of the isopropyl ether blends, both leaded and unleaded, appears unimpaired.

Table 3 gives pertinent inspection data on blended fuels containing 3 cc. of tetraethyl lead and meeting 100 octane number specifications. Specifications for the United States Army, United States Navy, British Air Ministry, Pratt & Whitney, and Wright Aeronautical Corporation are shown to allow comparison with fuel inspection. A typical aviation gasoline is also included for comparison. It will be observed from Table 3 that a 40 percent blend of isopropyl ether in aviation gasoline, with 3 cc. of lead per gallon of blend, meets the specifications set by the United States Army, United States Navy, British Air Ministry, Pratt & Whitney and Wright Aeronautical Corporation.

Figure 1 gives A.S.T.M. distillation for these same blends and the aviation gasoline.

Figure 2 shows how various 45 percent combination blends of technical iso-octane and isopropyl ether in aviation gasoline can be used to give a

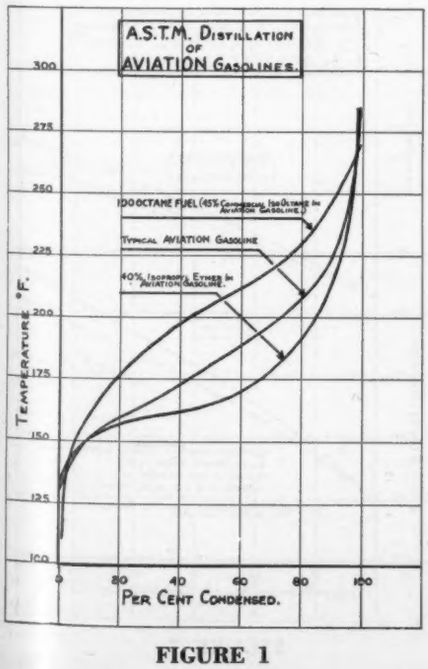


FIGURE 1

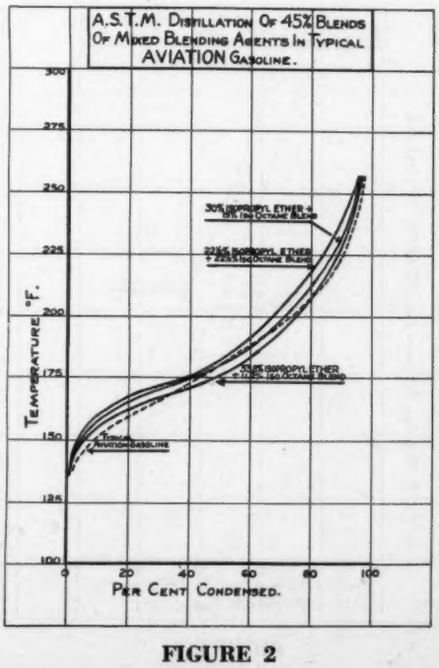

A.S.T.M. Distillation Of 45% Blends Of Mixed Blending Agents In Typical Aviation Gasoline.
Temperature °F.
Per Cent Condensed.

FIGURE 2

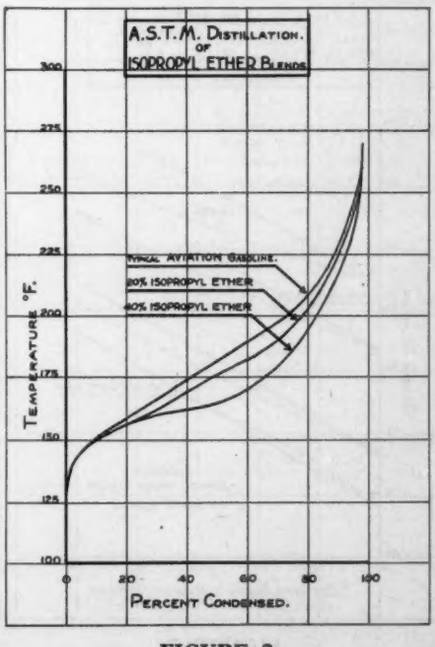


FIGURE 3

TABLE IV

Single Cylinder Octane Number Data for Blends in Aviation Gasoline of 74 C.F.R.-M.M.

Blending Agent	Volume Percent Added	A. S. T. M. OCTANE NUMBERS				Army Octane Number	Series 30 at 375°F. Octane Numbers
		Clear	1 cc. Ethyl Lead/Gallon	3 cc. Ethyl Lead/Gallon	Clear Blending Value	3 cc Ethyl Lead/Gallon	Clear
Isopropyl Ether	..	73.5	82.0	87.5	....	....	69
Isopropyl Ether	10	76.3	84.1	89.3	102	....	72
Isopropyl Ether	25	80.5	88.6	94.0	101	....	78
Isopropyl Ether	40	85.0	....	97.5	102	100	82
Iso-Octane	0	73.5	82.0	87.5	....	....	69
Iso-Octane	10	76.0	84.0	89.0	99	....	72
Iso-Octane	25	79.4	86.8	91.4	97	....	76
Iso-Octane	40	83.0	....	94.2	97	99	80
Iso-Octane	50	85.5	93.0	96.0	98	....	82

distillation very closely approximating the straight aviation gasoline distillation.

Figure 3 shows the distillation effect of various percentages of isopropyl ether in aviation gasoline and demonstrates that mid-range volatility may be varied widely without materially affecting overall boiling range of the gasoline.

OCTANE NUMBERS

A considerable amount of data is available in regard to the octane number and lead susceptibility of blends of isopropyl ether by various methods. Summarized data are shown in Tables 4 and 5 and graphically in Figures 4 to 7. A study of these results justifies the following conclusions in regard to performance on single cylinder test engines:

(a) Blended in commercial aviation gasolines, a fuel of 100 Army octane is possible with 40 percent of isopropyl ether without exceeding 3 cc. of lead tetraethyl.

(b) The blending value of isopropyl ether is slightly superior to the blending value of technical iso-octane in unleaded blends and also superior for any fixed amount of lead tetraethyl in the corresponding blends.

(c) The amount of lead tetraethyl necessary to meet a given octane number is less for isopropyl ether than for technical iso-octane in blends containing the same percentage concentrations.

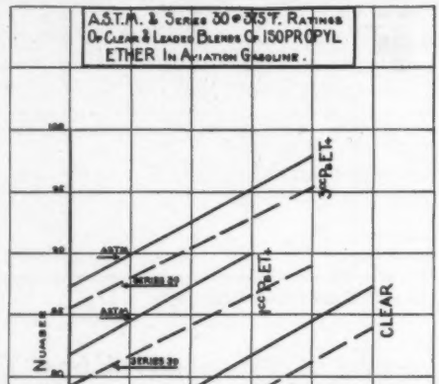

A.S.T.M. & Series 30 @ 375°F. Ratings Of Clear & Leaded Blends Of Isopropyl Ether In Aviation Gasoline.
Octane Numbers
Per Cent Isopropyl Ether In Aviation Gasoline.
CLEAR

FIGURE 4

ECONOMY

The question of cruising range possible with various fuels naturally raises the question of the limitation of isopropyl ether blends due to its 5-6 percent lower heat of combustion on a volume basis. Offhand it would appear that the range would be reduced correspondingly for a given tank capacity. This is not necessarily the case. It has already been pointed out that increasing compression ratio permits of operating at leaner air fuel mixtures. It has also been shown that the maximum Army octane number of a blend containing not over 3 cc. of lead per gallon is about 4 points higher for the isopropyl ether than for the corresponding technical iso-octane blend. Data are lacking on actual performance but from the

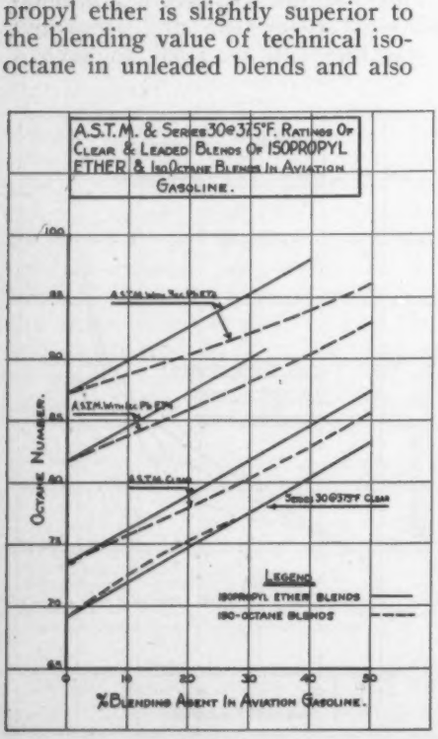

A.S.T.M. & Series 30 @ 375°F. Ratings Of Clear & Leaded Blends Of Isopropyl Ether & Iso Octane Blends In Aviation Gasoline.
Octane Number.
Legend
Isopropyl Ether Blends
Iso-Octane Blends
% Blending Agent In Aviation Gasoline.

FIGURE 5

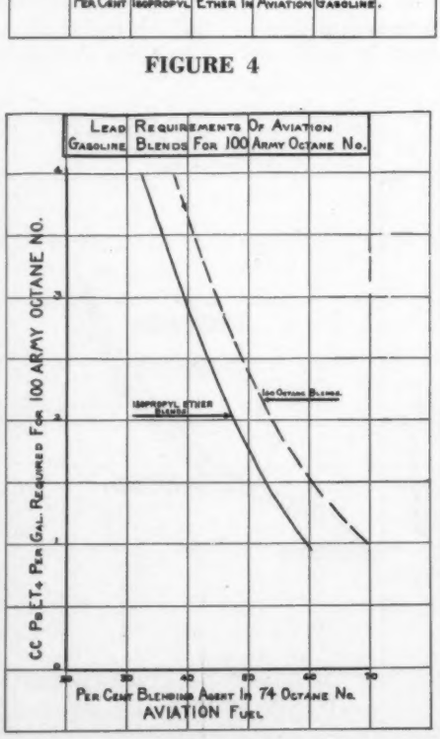

Lead Requirements Of Aviation Gasoline Blends For 100 Army Octane No.
CC P.b.E.t. Per Gal. Required For 100 Army Octane No.
Isopropyl Ether Blends
Iso Octane Blends
Per Cent Blending Agent In 74 Octane No. Aviation Fuel

FIGURE 6

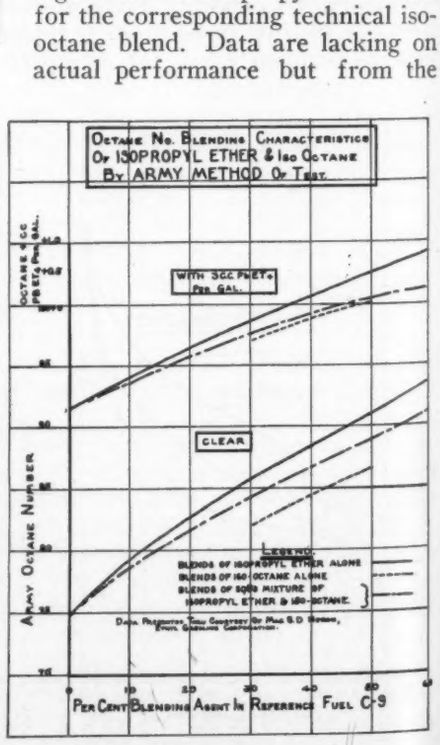

Octane No. Blending Characteristics Of Isopropyl Ether & Iso Octane By Army Method Of Test.
With 3 cc. P.b.E.t. Per Gal.
Clear
Army Octane Number
Per Cent Blending Agent In Reference Fuel C-9

FIGURE 7

TABLE V
Single Cylinder Army Octane Numbers of Blends of Isopropyl Ether and Technical Iso-octane in Knock Reference Fuel C-9

BLENDS OF REFERENCE FUEL C-9		OCTANE NUMBERS BY ARMY METHOD		
Volume Percent of Isopropyl Ether	Volume Percent of Crude Iso-Octane	Clear	With 3 cc. Tetraethyl Lead/Gallon	Clear Blending Value of Blending Agent
..	..	74.8	93.0	...
10	..	79.0	94.0	117
20	..	82.7	96.6	114
30	..	85.7	98.4	111
40	..	88.3	Equals Iso-Octane + 0.18 cc. Lead	109
50	..	90.6	Equals Iso-Octane + 0.44 cc. Lead	106
60	..	93.5	Equals Iso-Octane + 0.82 cc. Lead	106
5	5	77.8	93.6	105
10	10	81.5	96.0	108
15	15	84.1	97.6	106
20	20	86.7	99.2	105
25	25	88.8	Equals Iso-Octane + 0.08 cc. Lead	103
30	30	91.0	Equals Iso-Octane + 0.22 cc. Lead	102
..	30	82.0	97.0	99
..	40	84.4	98.7	99
..	50	86.5	Equals Iso-Octane + 0.05 cc. Lead	98

(Data obtained through the courtesy of Major S. D. Heron, Ethyl Gasoline Corporation.)

best figures available it would appear that compression ratio could be increased—or possibly supercharger boost increased—to permit of operating at about a 10 percent lower specific fuel consumption, thus compensating for the lower heating value. There are indications also that for equal 100 Army octane rating fuels, the isopropyl ether blend will permit of a leaner mixture without exceeding critical head temperature—and providing compression ratio is high enough to permit of very lean mixtures—again compensating for its inherently lower heating value. Needless to state this discussion applies only to comparisons with 100 percent hydrocarbon fuels of 100 Army octane number. The isopropyl ether blends of 100 Army octane numbers are far superior to all fuels of lower octane number.

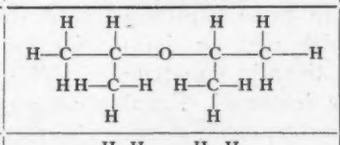
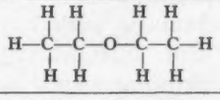
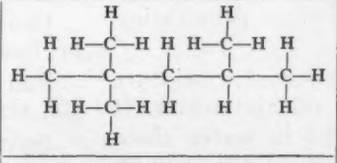
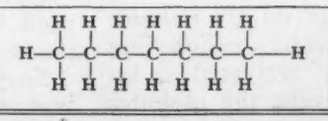
AVAILABILITY

Of particular interest when proposing a new and different fuel is the question of potential supplies of raw materials as related to potential demand. The total United States consumption for all grades of aviation fuels was 63,000,000 gallons for 1934 and is estimated as 88,500,000 gallons for 1936.

A recent survey of potential supplies of propylene, the raw material for making isopropyl ether, has shown that in this country, sufficient is available exclusive of all other normal demands for other purposes, to produce at the present time approximately 340,000,000 gallons per year of technical isopropyl ether. Assuming that 100 octane fuel is required (using 3 cc. lead/gallon), this is sufficient to produce some 850,000,000 gallons per year of finished product. Thus it is apparent that the availability of this fuel is much more than sufficient to meet the entire requirements for 100 octane gasoline even in the event of national emergency. When combined with the available supplies of technical iso-octane, estimated at 155,000,000 gallons per year, there is every assurance that adequate quantities will be available immediately for any demand. The cost of the material for large production is entirely reasonable.

When isopropyl ether and iso-octane are available, blends of the two offer certain advantages lacking in either when used separately, particularly with respect to volatility. Data have been presented which show that a 50-50 blend of the two in Standard knock reference fuel C-9 has an anti-knock value superior to that obtained when using iso-octane alone as the blending agent. By using such blends a fairly wide range of volatilities is made available

(Continued on page 317)

COMPOUND	Chemical Formula	Boiling Point °F.	A. S. T. M. Octane No. (Clear Blending Value When Blended 25% in Aviation Gasoline)
Isopropyl Ether ($C_6H_{14}O$)		154	About 100
Ethyl Ether ($C_4H_{10}O$)		94	Below 0
Iso-Octane (C_8H_{18})		211	100
n Heptane (C_7H_{16})		211	0

Asphalt Emulsions . . .

J. W. SMITH
Chief Engineer, Berry Asphalt Company

ASPHALT emulsions are a mixture of asphalt and water in which an asphalt of practically any required physical characteristics, i.e., penteration, softening point, ductility, etc., may be mechanically combined with water in such a way that the resultant product may be utilized at normal temperatures. After a suitable time period the water will leave the mixture, leaving the asphalt with approximately its original characteristics.

This ability of the emulsion obviously has decided advantages in many cases; for example, the waterproofing of insulation is best accomplished with a thin layer of asphalt of a normal softening point of 160 to 180°F. At normal temperature this asphalt is solid, and for application it would be necessary to heat it to approximately 350°F. At this temperature it may be mopped on, but the job is difficult and the final appearance unworkmanlike. In contract, the same asphalt may be obtained as an emulsion which may be troweled on, or may be thinned and brushed on. Quite evidently the ease of application, and neatness of the job, are desirable. In applying a 60 penetration paving cement to sand and stone aggregate for the manufacture of paving cement it is necessary to heat not only the asphalt but the entire amount of sand and stone must also be heated to insure uniform coating of the aggregate. This paving mixture must then be laid while still hot, and compacted, all at a temperature above 300°F.

In contrast, by using emulsion, the aggregate may be cold, and may even be wet, and the emulsion is used cold. The two may be mixed in a pug mill, as is the hot mix, or as is less costly, aggregate may be spread on the road, the emulsion sprayed over it, and mixing is completed by passing a road blade over the mass several times.

Emulsions and cutback asphalt are somewhat in competition in that one is probably as satisfactory as the other on most jobs in which either is suitable. This is more generally true in road emulsions and cutbacks, than in industrial usages. However, there are considerable differences in their handling. Emulsions may be used safely with wet or damp aggregate, and consequently down time in construction, due to inclement weather is lessened. Emulsion is far more desirable as a waterproofing material, in that a better bond usually is obtained with this material than either cutback or hot asphalt. However, emulsion is not suitable as a priming coat on pavements since it breaks out before penetrating satisfactorily.

An oil and water emulsion consists of a mixture of very finely divided particles of oil and water. It can be of two general types, the oil in water class, in which minutely small globules of oil are individually surrounded by a film of water, which film has in some way been chemically activated to increase its surface tension and prevent the globules of oil from coalescing, or it may be of the water-in-oil type, in which the water globules are surrounded by the oil film.

Probably all producers and refiners of crude oil are familiar with emulsions, which can, and do, occur with oil, at any stage from its production from the ground, to its use as finished material. Producers of crude oil spend a great amount of money and effort to prevent the formation of emulsions, and to break down emulsions the formation of which they can not prevent. Some refiners of crude oil have the same difficulty, since at any point in the processing of the oil, should it be agitated in the presence of water, a certain amount of emulsion may be made. Most of these emulsions are of the water in oil type, in which the water is surrounded by oil. This type is not of commercial value and is not as a rule manufactured.

The other type, the oil in water emulsion has many uses, such as for industrial coatings and paints, road building, etc., when used with asphalt as the oil. This type is also used in the drug business, the manufacture of cutting oils, and many other specialties. All of these emulsions are manufactured by dispersing the oil in water, which must be treated in some way to increase its surface tension in order to prevent the recombining of the small particles of oil.

Asphaltic emulsions are of two general classes, in one of which the retardant is a finely divided clay or bentonite, and in the other it is a soap of some kind. The first class is largely used in industrial emulsions, such as waterproofing and paints. The latter is used largely for road building. The balance of this article deals with the manufacture and use of the latter type.

A discussion of suitable equipment for the manufacture of soap type emulsion follows:

The actual plant required to manufacture the soap emulsions is simple, both in construction and in operation. The requirements are: measuring tanks and manufacturing kettle for the soap, pumps, dispersing mill and storage tanks. Reference to the layout drawing, Figure 1, is as follows:

Pan A contains steam coils for rosin, which must be handled while hot.

Pan B contains caustic soda of approximately 30° Be. strength.

Boxes C and D are calibrated accurately, and are used to measure the melted rosin and caustic into the soap kettle E.

Soap kettle E must be steam jacketed, and it is best equipped with a paddle type agitator. In the

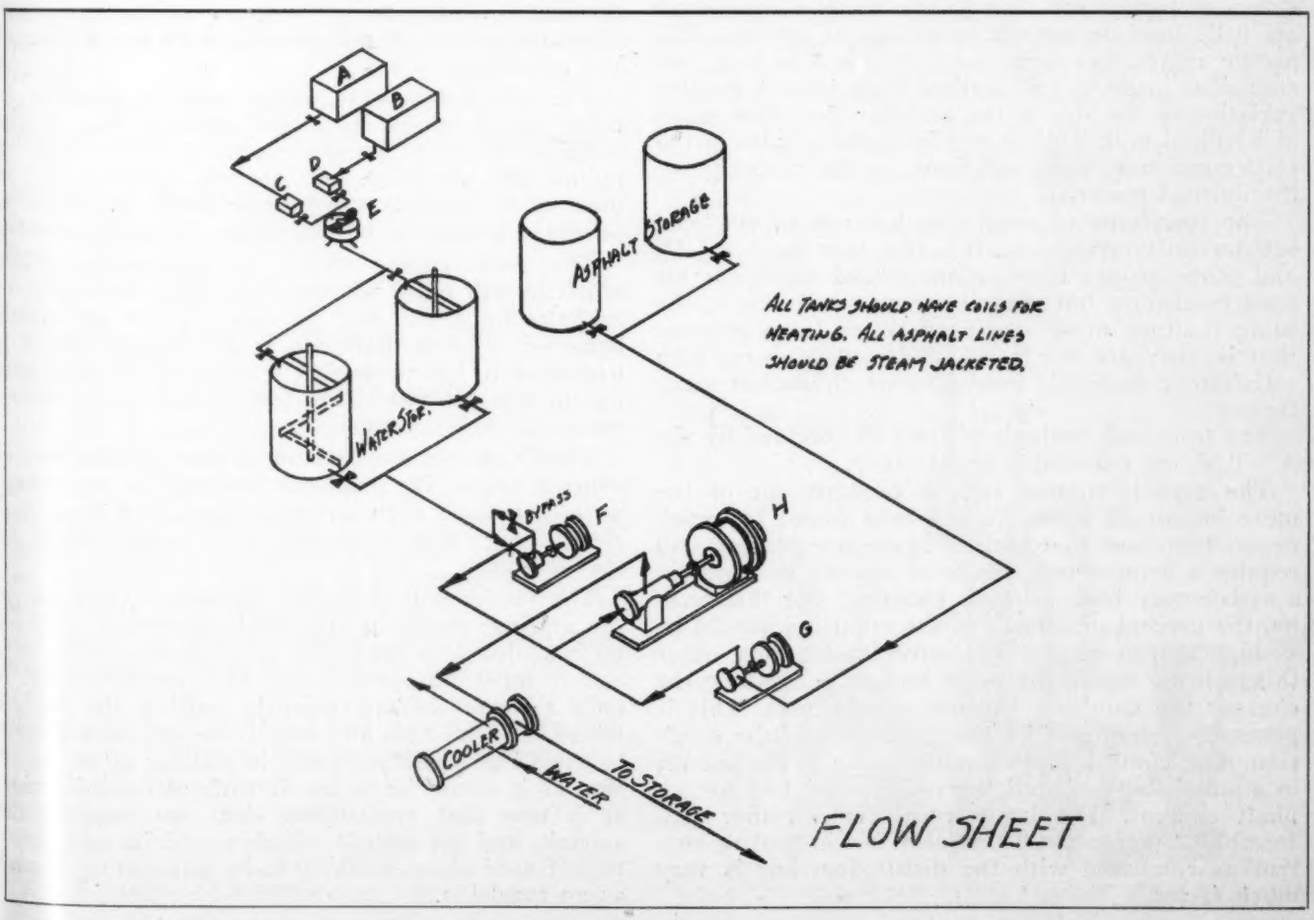
manufacture of the soap, the required amount of caustic solution measured out through the box D is heated to the boiling point in the kettle. The rosin is added slowly to the caustic at this point, with continuous agitation. The temperature must be watched carefully, as it is necessary to have the solution boiling for the reaction to take place; if too hot, foaming will occur. After all of the rosin is added, a few minutes additional cooking is sufficient to complete the batch, after which it is pumped to the water tank and mixed with water. It generally is advisable to heat the water to about 120°F. before adding the soap to assist getting the soap into solution.

The net percentages of rosin and caustic will vary slightly, depending on the type of rosin, the pH of the water being used, and the amount of salt in the asphalt. A reasonable formula would consist of 87 pounds rosin, 13 pounds caustic as Na_2O and 50 pounds water. The amount of water used in the manufacture of the soap is unimportant—it being only a carrier for the caustic. This formula makes soap for a normal summer emulsion. For a quick-break type approximately 1 percent of the total water used should be rosin plus caustic, i.e.: 0.87 percent rosin, 0.13 percent caustic, based on the total water used in the finished emulsions. For a slow break emulsion these should be increased to about 5 percent, so that of the total water, rosin would be 4.35 percent and Na_2O 0.65 percent. The demulsibility of the emulsion may be varied by means of the percentage of soap added, the lower the quantity of soap, the higher the demulsibility. Some change in the viscosity of the finished product may be obtained by varying the openings at the colloid mill, but better control of this characteristic is obtained by varying the percentage of caustic in the soap. Emulsion manufactured with this soap will freeze and break out in winter weather. For temperatures below 30°F. a winter emulsion must be used, requiring a different soap base. One satisfactory material which may be used for this type of emulsion is a soap made from potassium hydroxide and pine tar.

Various other ingredients may be used to replace the rosin, as saponifiable animal or vegetable oil is the only requirement. Under present market prices, however, rosin is the cheapest material.

Pumps F and G are respectively the water and asphalt pumps. These are preferably of the rotary type, with positive displacement, as by means of these pumps the percentages of the two materials is measured. The pumps may be of the same size, in which case the water-soap pump is arranged with a by-pass from the discharge back to the suction, with a needle point globe valve for regulation. With both pumps operating full, the resulting emulsion will be 50 percent water and reagent and 50 percent asphalt. This requires opening the by-pass valve of the water-soap pump a certain amount in order to manufacture emulsion with more than 50 percent asphalt content. While some refiners might consider this a rather crude method, it has been found to work out well in practice, giving an error on the finished material of less than 1 percent.

The asphalt and water-soap solution meet at a tee and dispersion is completed in the mill H. Although



this mill may be of several types, a satisfactory mill is the heart of the plant. While it consists merely of a plane or cylinder revolving at a high speed against a fixed face the design is quite technical. Some mills have a corrugated rotating face and give the material a mixing action along with the shearing force. Others have smooth faces and the dispersing force is only the hydraulic shear developed. This latter type runs at somewhat higher peripheral speeds than the former.

Another type of dispersing mill consists of a rotating cone set at a clearance of from .010 to .050 inches from a fixed face. The material passes through this opening, during which time the dispersal is completed. Considerable heat is generated in this operation, and the mill should be water-jacketed. The mill should be designed so that the rotor clearance is adjustable by means of a hand-wheel or ring. The clearance affects the power requirement greatly, and this item is rather high at the normal operating speed of 3500 r.p.m.

Size of Mill Gal./Hour	R.P.M.	H.P. Required
20-100	3600	5-10
300-500	3600	35-40
500-1000	3600	40-50
1000-5000	3600	75-100

The capacity of the mill is determined by the type material desired. For fine materials, the throughput of the mill must be reduced.

Most types of colloid mills have been patented. Among other methods of complete dispersion are the homogenizing valve and the paddle mixer. These have been used with much success in the emulsification of lighter oils, but to the writer's knowledge are little used on asphalt emulsions at present. The paddle mixer has been used to some extent, but emulsions made by this method have a much greater variation in the size of the globules than that made in a colloid mill. This causes irregular results in the settlement test, and variations in the viscosity of the finished material.

The specifying of emulsions has not as yet been satisfactorily established. It is true that the A.S.T.M. and other groups have recommended standards for road emulsions, but these have, to some extent, the same fault as most specifications of large groups; that is, they are too broad, and include along with satisfactory materials emulsions which are not satisfactory.

The tests and methods of tests as specified by the A.S.T.M. are reasonably satisfactory.

The asphalt content test, is perhaps one of the more important items. It has been found by much experimentation, that a given aggregate grading will require a definite percentage of asphalt to maintain a satisfactory bond without bleeding. For this reason, the percent of asphalt in the emulsion should be as high as can be worked conveniently, since other things being equal, the more asphalt percentage the cheaper the emulsion becomes to the user. This is generally determined by the distillation of the emulsion. For control purposes the water is cooked off in a small flat pan, and the residue weighed for asphalt content. The latter result runs rather uniformly 0.3 percent to 0.5 percent low in asphalt content as compared with the distillation, but is very much faster.

The viscosity of the emulsion is of importance since it determines the ease of handling the material. At present most of the high asphalt content grades are specified as having to flow from the bung of a drum. For a few purposes this may be permitted, but it is probable that this viscous a material will not be satisfactory in most cases. The purchaser wants a high asphalt content, and the manufacturer in making this must see-saw between high viscosity which is hard to handle and settlement, if he makes low viscosity material. It appears difficult to strike a satisfactory balance in these two items, unless the asphalt content is reduced, which in turn the purchaser does not like. The viscosity usually is run in the Saybolt furol viscosimeter, although for control, some manufacturers use a calibrated glass pipette.

The demulsibility test determines the behavior of the emulsion on the road. For plant mixing and for road mixing, a slow-break material is required, which permits thorough coating of the aggregate, spreading, and rolling before the emulsion breaks. For seal coat, a quick-break emulsion is desirable.

The settlement test is a measure of stability of the emulsions, and to a large extent is given greater importance than it justifies. While it is true that the buyer does not want an emulsion which is separated into oil and water, a settlement requirement of 5 percent in 5 days is much closer than the use in general requires, inasmuch as a very slight agitation will prevent this settlement. The movement of the tank car from manufacturer to job is sufficient to keep the material entirely uniform, and the car nearly always is used before settlement can take place to any appreciable extent. This test appears rather like the color test of gasoline. It was a good idea when most suppliers could not meet it, as it permitted selling exclusive specifications but when all manufacturers could meet it, there was no longer any advantage in it.

The miscibility with water test is required in many specifications, quite often without reason. The addition of water to the emulsion serves only to reduce the viscosity—and asphalt content—and in most cases, the buyer would be much better off to purchase a material of the proper viscosity initially.

The stone-coating test is of importance. While much is still to be learned regarding the action of asphalts on stone, and the reasons for the erratic behavior of some materials, it is admitted that it is necessary to have complete coating of the aggregate by the asphalt film. This test insures such coating when properly specified.

The sieve test is a measure of the completeness of emulsification. Its practical meaning is the avoidance of trouble with screens, pumps and spray nozzles in use, and it should be incorporated in all specifications.

The reader will note that the above tests are on the original emulsion only. This discussion will not go into detail in regard to quality of asphalt used, but it must be remembered that emulsification is only a means of conveniently getting the asphalt where it is wanted, and that it is just as necessary to use a high-quality asphalt in making up the emulsion as it would be to use it without emulsification. It is true that emulsifying does not improve the asphalt, and no asphalt which would be unsatisfactory if used alone, is likely to be satisfactory if used as an emulsion.

Combustion

Characteristics of Fuels

A. W. TRUSTY,

Chief Chemist, Louisiana Oil Refining Corporation

SINCE the beginning of the refining industry, the transition in fuels has been from solid to liquid to gaseous; the leadership was first held by coal, then by oil and now is held by gas. In 1933, 54.7 percent of the total heat units generated came from gas, 39 percent from oil (including acid sludge) and 6.3 percent from coal and coke.

The fuel efficiency at refineries has been increasing in recent years. In 1925 the average B.t.u. consumed per barrel of crude was 840,000; in 1929, 640,000; in 1933, 660,000 B.t.u. The improvement in fuel economy is closely related to increase in crude runs to stills. Another factor which has influenced fuel economy in the past is the trend in cracking, a process requiring more than the average expenditure of heat. However, the technique of heat exchange and combustion has improved, and the future should see some reduction in fuel consumption.

CHEMISTRY OF COMBUSTION

The constituents of fuel—solid, liquid, gaseous, include carbon, hydrogen, hydrocarbons, oxygen, nitrogen, sulphur, ash and water.

The carbon burns to carbon dioxide if sufficient air is present, liberating 14,600 B.t.u. per pound of carbon.

$C+O_2=CO_2+14{,}600$ B.t.u. per pound.

If insufficient air is present, carbon monoxide is formed:

$2C+O_2=2\ CO+4450$ B.t.u. per pound.

The carbon monoxide can be burned if more air is supplied:

$2CO+O_2=2CO_2+4350^*$ B.t.u. per pound.

Hydrogen burns to form water vapor, liberating heat as follows:

$2H_2+O_2=2H_2O+62{,}100$ B.t.u. per pound.

Sulphur, if present in the free state, or if chemically combined with hydrocarbons, burns to liberate 4050 B.t.u. of heat per pound.

$S+O_2=SO_2+4050$ B.t.u. of heat per pound.

If the sulphur in a coke or coal is found in the form of calcium sulphate, iron sulphate, etc., of course it has no heating value.

Nitrogen, present in varying amounts in practically all fuels, is inert, and takes no part in the combustion.

Hydrocarbons burn to form carbon dioxide and water vapor, liberating heat depending on the chemical analysis. For example:

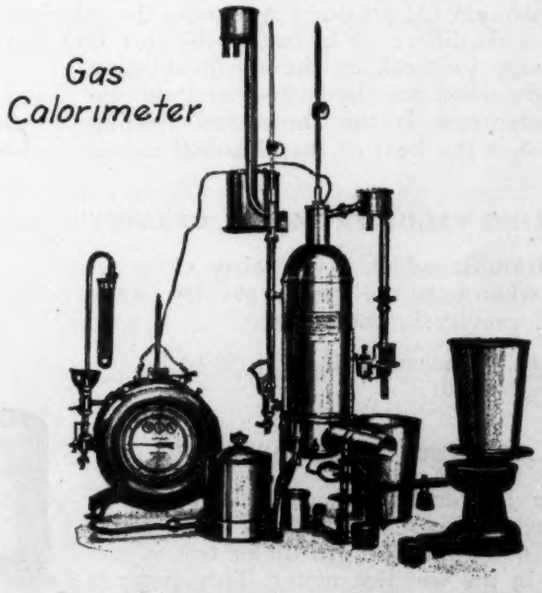
$C_{11}H_{24}+34\ O_2=11\ CO_2+12\ H_2O$

The most important factor in any fuel is the heating value. This value may be determined by a calorimeter test, by calculation from the chemical analysis, or by a formula if only the A.P.I. gravity is known.

CALORIMETER DETERMINATION

For liquid or solid fuels the bomb calorimeter is used. It consists of a small steel alloy vessel or bomb built for high pressure and to resist acid corrosion. In this bomb a small known weight (1 to 2 grams) of fuel is burned in an atmosphere of dense oxygen, while the instrument is submerged in a known quantity of water which absorbs the heat of combustion.

The fuel is weighed into a small alloy metal crucible, placed on a support, and a fine, iron fuse wire is attached to the two terminals in the bomb and passed through the sample of oil or coal. The top of the bomb is screwed in place, about 450 pounds per square inch of pressure applied from an oxygen drum, and the bomb is immersed in a bucket containing exactly 2000 grams of water. The bucket is insulated with an air bath in order to reduce radiation losses. An accurate thermometer is suspended in the water. Electrical connection is made and the fuel is burned. For example, the rise in temperature of the water (corrected for radiation) is 2.53°C.



*10,050 B.t.u. per pound of carbon.

The charge of fuel burned was 1.4784 grams. The heating value is

$$\frac{3.53 \times \text{water equivalent of calorimeter} \times 1.8}{1.4784} = \text{Bt.u. per lb.}$$

Note: The "water equivalent" is determined for each calorimeter by standardizing with standard combustion samples supplied by the United States Bureau of Standards.

HEATING VALUE FROM CHEMICAL ANALYSIS

In many cases the chemical analysis of a fuel is obtainable more easily than a calorimeter test, and the heating value of a solid fued may be approximated very closely by the use of Dulong's formula:

$$Q = 14{,}600\ C + 62{,}100\ \left(H - \frac{O}{8}\right) + 400\ S \qquad (1)$$

Where Q is the heating value in B.t.u. per pound, C, H, O and S are the percentages, expressed in decimal parts of the total weight of the fuel, of carbon, hydrogen, oxygen and sulfur, respectively.

For example a refinery coke with the analysis:

Carbon	.96 percent
Hydrogen	.021
Sulfur	.41
Ash	.29

B.t.u./lb. 15231 (calorimeter test).

$$\text{B.t.u. per pound} = 14{,}600\ (.96) + 62{,}100\ (.021) + 400\ (9.0041) = 15{,}307$$

For liquid or gaseous hydrocarbons the following approximate formula seems to give results which check to the calorimeter test closely.

$$Q = 14{,}600\ C + 52{,}300\ \left(H - \frac{O}{8}\right) \qquad (2)$$

If formula (1) be applied to methane, for instance, the heating value is calculated as follows:

CH_4 contains 75 percent carbon and 25 percent hydrogen by weight.

$.75 \times 14{,}600 + .25 \times 62{,}100 = 24{,}008$ B.t.u. per pound or 1034 B.t.u. per cubic foot.

By formula (2)

$Q = 14{,}600\ (.75) + 52{,}300\ (.25) = 24{,}008$ B.t.u. per pound or 1014 B.t.u. per cu. ft.

Formula (1) gives a result that is much higher and Formula (2) a value that checks the calorimetric tests. This difference is due to the fact that heat is necessary to break up the chemical union of the carbon and hydrogen, and the calorimeter test is the theoretical heating value less the heat of the chemical union.

HEATING VALUE FROM A.P.I. GRAVITY

A formula which gives fairly close results when only the specific gravity of the A.P.I. gravity is known is

B.t.u. per pound = 18,650 + 40 (A.P.I. gravity—10)

HEATING VALUE OF GASES

The Junker type Calorimeter is one of the best known for finding the heating value of gases. The gas under test is metered in the wet test meter. This meter is equipped with a presure gauge, a thermometer, and a bell which strikes at each revolution of the large pointer. From the meter the gas passes through a pressure regulator between the meter and burner. The burner is of the Bunsen type, and is equipped with a micrometer cock. Three adjustable baffle plates are supplied to prevent downward radiation and consequent loss of heat from the combustion chamber.

The calorimeter proper consists of a central combustion chamber around which is located the water heating element consisting of 40 tinned copper tubes arranged in two staggered concentric rows. The hot gases leaving the burner pass up through the heating element and out of the flue at the bottom on the right side.

The water enters the calorimeter through an inlet weir at the left, and passes out through a similar weir at the right. The flow is adjusted through a micrometer cock on the inlet, and is passed to the weighing bucket or diverted to the waste through a three-way cock on the outlet. The temperatures of the inlet and outlet water are read by means of two thermometers. These are graduated to one-tenth of a degree, and are equipped with microscopic sights.

If the increase in temperature of water is observed, the heat generated per pound of fuel will be obtained from the equation:

$$Q = \frac{W\ (T_2 - T)}{L}$$

Where W is the weight of the cooling water, T_2—T its increase in temperature and L the weight of the fuel burned.

Or if the heating value is desired on the basis of volume, the formula:

$$HV = \frac{WT}{V} \text{ can be used,}$$

Where W is the pounds of water heated, T is the average

Bomb Calorimeter

TABLE I

Data on Common Fuels

	Chemical Symbol	Molecular Weight	Weight /Cu. Ft. at 14.7lb, 60°F.	B.t.u. Pound		B.t.u. /Cu. Ft.		Required Weight of Air/lb Fuel	Cu. Ft. of Air Required For Combustion/ lb Gas	Cu. Ft. of Air Required For Combustion/ Cu.Ft. Gas
				High	Low	High	Low			
Hydrogen	H_2	2	.00527lb	62100	52275	327	275	34.64	456	2.4
Carbon	C	12	.....	14600	14600	.....	.....	11.56	152	....
Oxygen	O_2	32	.0842	.....	.....	.....	.....	....	....	....
Nitrogen	N_2	28	.0738	.....	.....	.....	.....	....	....	....
Carbon Dioxide	CO_2	44	.1159	.....	.....	.....	.....	....	....	....
Carbon Monoxide	CO	28	.0738	4380	4380	324	324	2.48	33	2.4
Methane	CH_4	16	.0422	24000	21544	1013	910	17.32	228	9.61
Ethane	C_2H_6	30	.0790	22340	20375	1800	1620	16.16	213	16.83
Propane	C_3H_8	44	.1162	21420	19630	2500	2281	15.8	208	24.17
N-Butane	C_4H_{10}	58	.1531	21122	19427	3234	2964	15.55	205	31.39
Ethylene	C_2H_4	28	.0738	21900	21496	1615	1512	14.85	195	14.3
Acetylene	C_2H_2	26	.0685	21860	21094	1500	1440	13.32	175	12
Benzene	C_6H_6	78	.2055	18100	17343	3720	3560	13.32	175	36

	Weight of Combustion Products Per Pound of Gas			Volume of Combustion Products Per Pound of Gas at 60°F.		
	CO_2	H_2O	N_2	CO_2	H_2O	N_2
Hydrogen	.....	9.0lb	26.64lb	.....	187 Cu. Ft.	362 Cu. Ft.
Carbon	3.67	.....	8.89	31.6	.....	120
Carbon Monoxide	1.57	.....	1.91	13.5	.....	25.8
Methane	2.75	2.25	13.32	23.6	47.2	180
Ethane	2.93	1.80	12.43	25.2	37.8	168
Propane	3.00	1.64	12.16	25.5	34.5	164.5
N-Butane	3.04	1.55	11.96	26.2	32.6	161.5
Ethylene	3.14	1.29	11.42	27.0	27.0	164
Acetylene	3.39	.69	10.24	29.2	14.55	138
Benzene	3.39	.69	10.24	29.2	14.55	138

temperature difference of inlet and outlet water, F., V is the corrected volume of gas burned, in cubic feet, H is the B.t.u. per cubic foot.

HEATING VALUE OF GAS MIXTURES

For example, calculate the heating value of a natural gas with the following low temperature distillation analysis:

Component	Percent by gas volume		B.t.u. per cu. ft.	
Methane	55 or .55	×	1008	= 554.4
Ethane	20 or .20	×	1763	= 352.6
Propane	10 or .10	×	2518	= 251.8
N-butane	9 or .09	×	3260	= 293.0
Nitrogen	5 or .05	×	0	= 0
				1451.8

or 1452 B.t.u. per cubic foot of gas.

HIGH AND LOW HEATING VALUE

Any fuel containing hydrogen will have a *higher* and a *lower* heating value, and the latter is always found by subtracting from the former the latent heat in the steam formed by the combustion of hydrogen in the fuel.

For example, octane, C_8H_{18}, containing 84.6 percent carbon and 15.4 percent hydrogen.

B.t.u. per pound = .846 (14,600) + .154 (52,300) = 20,406

The amount of steam formed on combustion is .154 × 9 lbs. = 1.386 pounds. The latent heat of this amount of steam is 1.386 × 970 = 1344 B.t.u.

Therefore the lower heating value is 20,406 — 1344 = 19,062.

Since the products of combustion in a calorimeter are always cooled below 212°F., and the water vapor is condensed, the high or gross heating value is the value reported in all calorimetric tests.

AIR REQUIRED FOR COMBUSTION

When carbon burns completely, carbon dioxide is formed:

$$\underset{12}{C} + \underset{32}{O_2} = \underset{44}{CO_2}$$

The numbers refer to the atomic weights of the elements, and they show that 12 parts of carbon, by weight, unite with 32 parts of oxygen to form 44 parts of carbon dioxide. Thus, for each pound of carbon burned, there are required $\frac{32}{12}$ or 2.67 pounds of oxygen.

When hydrogen is burned we have the chemical equation:

$$\underset{4}{2\,H_2} + \underset{32}{O_2} = \underset{36}{2\,H_2O}$$

showing that 1 pound of hydrogen unites with 8 pounds of oxygen forming 9 pounds of water.

A general equation for the oxygen required for the combustion of any fuel:

2.667 C + 8 H = pounds of oxygen per pound of fuel

where C and H are the proportions, by weight, of carbon, and hydrogen in the fuel.

Air is composed principally of oxygen and nitrogen in the following proportions:

	Weight	Volume
Oxygen	23.1 percent	21 percent
Nitrogen	76.9 percent	79 percent

A formula for the air required for the combustion of any fuel:

$$11.6\,C + 34.63\,(H - \frac{O}{8}) + .0432\,S = \text{lbs. of air per lb. of fuel}$$

where C, H, O and S represent the percentage by weight of carbon, hydrogen, oxygen and sulfur respectively.

For example, the air required for methane, which

is the largest constituent of natural gas, would be as follows:

CH_4 contains 25 percent hydrogen and 75 percent carbon, by weight,

11.6 (.75) + 34.63 (.25) = 17.35 pounds of air per pound of methane.

When fuels, such as alcohol, contain oxygen, this oxygen may be subtracted from the theoretical requirement, as the oxygen in the fuel unites with some of the hydrogen during combustion.

EXCESS AIR

It is impossible to burn a fuel completely with the theoretical amount of air. Usually about 40 percent excess air is used, in order to insure complete combustion and prevent waste heat from leaving the stack in the form of carbon monoxide.

FLAME TEMPERATURE

The maximum temperature of the products of combustion of a fuel, or the flame temperature, may be approximated from the formula:

$$\text{Temperature rise} = \frac{Q}{CW}$$

where Q is the lower heating value of the fuel, C is the mean specific heat of the products of combustion, and W is the weight of the products of combustion per pound of fuel. The actual temperature after combustion will be the sum of the original and the rise. For example, the flame temperature of methane:

$$\text{Temperature rise} = \frac{21{,}544}{18.32 \times .27} = 4370°\text{F.}$$

This temperature is never attained in practice. Due to radiation, excess air and other causes, the actual temperature is much lower than the theoretical. It is valuable to know the theoretical flame temperature of the various fuels when designing furnaces and for industrial heating.

IGNITION TEMPERATURE

The ignition temperature of a substance is the temperature at which the heat lost by conduction, etc., is more than counterbalanced by the rate at which it is developed by the reaction, the combustion thus becoming self-propellant. This temperature is a function not only of the gaseous mixture employed but also of the means used for heating it. Also, there is often a short "pre-flame" period, during which the combustion is autogenous, but without any actual appearance of flame.

The Equivalent Costs of Domestic Fuels
(For the same heat for Unit Cost)

Natural Gas At 900 B.t.u. Per Cu. Ft.	Domestic Coal at 12,000 B.t.u. per Pound	Oil Distillate At 140,000 B.t.u. per Gallon	Coal Gas 600 B.t.u. Per Cu. Ft.	Wood at 8,500 B.t.u. Per Pound	Electricity 3,415 B.t.u. Per K.W. Hour
Per M Cu. Ft.	Per Ton	Per Gallon	Per M Cu. Ft.	Per Cord	Per 1,000 H.P., Hr.
$ .10	$ 2.67	$0.0156	$0.07	$2.30	$0.28
.20	5.34	.0311	.13	4.60	.56
.30	8.00	.0467	.20	6.90	.84
.40	10.68	.0612	.26	9.20	1.12
.50	13.35	.0780	.34	11.50	1.40
.60	16.00	.0933	.40	13.80	1.75
.70	18.67	.1089	.47	16.10	2.00
.80	21.36	.1224	.52	18.40	2.27
.90	24.00	.1400	.60	20.70	2.55
1.00	26.70	.1560	.68	23.00	2.83

The ignition temperatures are lowest for paraffin and naphthenic hydrocarbons and highest for aromatics.

It is a well known fact that combustion will not take place simply by bringing fuel into contact with oxygen. Fuels are commonly stored in contact with air, and they do not burn. Hence it is evident that a supply of oxygen is not the only essential for combustion. The principal condition is that of temperature. Every combustible substance has a definite temperature known as its ignition temperature, to which it must be raised in order to burn.

The ignition temperature of some of the common gases and fuels are as follows:

Hydrogen	1110°F.
Hydrogen sulphide	665°F.
Methane	1275°F.
Acetylene	750°F.
Ethylene	1005°F.
Ethane	1050°F.
Propane	1010°F.
Butane	1000°F.
Pentane	985°F.
Paraffin	500°F.
Sulphur	470°F.
Coal	760-925°F.

Pressure tends to lower the ignition temperature. This effect is utilized in a Diesel engine, where the pressure lowers the temperature of combustion considerably. Moisture tends to raise the ignition temperature; the maximum effect of moisture is about 75-100°F.

LIMITS OF INFLAMMABILITY

The combustible limits of most petroleum vapors lie between 1 and 6 percent. When the percentage of vapor in the air-vapor mixture is less than 1 percent, there is insufficient of the inflammable ingredient to support combustion. If the percentage of vapor is in excess of 6 percent, there is insufficient oxygen in the confined space to permit combustion to continue. As the percentage of vapor in the air-vapor mixture approaches the mid-point between 1 and 6 percent, the mixture is in a highly dangerous state and an explosion will occur if a source of heat is supplied, a spark, a flame, hot metal, etc., to raise the mixture to its ignition temperature.

The limits of inflammability are shown for some hydrocarbons:

The Equivalent Costs of Domestic Fuels
(For the Same Heat for Unit Cost)

Hydrocarbon	LIMIT OF INFLAMMABILITY Percent by Volume in air	
	Lower	Higher
Methane	5.6	14.8
Ethane	3.1	10.7
Propane	2.2	7.3
Butane	1.6	5.8
Pentane	1.4	4.5
Hexane	1.2	3.3
Gasolene	1.5	5.3

In comparing the relative costs of fuels, the costs of firing should also be considered. For instance, in burning fuel oil by steam atomization, the steam consumption is about .4 pounds of steam per pound of oil. Natural gas, due to its high heating value, ease of handling, low cost of burning, etc., makes the ideal fuel in refining areas where gas is available.

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Water-White Hydrocarbons *from* Trinidad Asphalt

HALLEY T. GAETZ*

IN a short report reference is briefly made to the preparation, fractionation, and property and analytical study of 25 water-white oily hydrocarbon fractions extracted from Trinidad Lake asphalt. A number of contributing features associated with the experimental research are also briefly discussed in respect to their relationship to former work in the fields of petroleums and bituminous substances. The writer is the author of the recent book "Water White Hydrocarbons from Trinidad Asphalt."

INTRODUCTION

THE detailed scientific study of such bituminous substances as Trinidad Lake asphalt is not new. Nevertheless, during the late nineteenth century the problem of separating asphaltic components was considered practically impossible, and considerable investigation in this field has thus far led to results both progressive, and yet confusing in many respects, at present knowledge of the exact chemical composition of asphalts being meagre indeed.

The preparation of water-white oily hydrocarbons from commercially refined Trinidad Lake asphalt has recently been briefly outlined in an earlier report[6], and more fully dealt with in a later book publication[7] which has been reviewed by this journal[16] and elsewhere[4], additional reviews now pending[17 22]. It was the purpose of the work, on a scientific basis, to purify to a permanently water-white condition as quantitatively as possible, the petrolene or oily hydrocarbons extracted from the asphalt, and to prepare them free from decomposition in order to later fractionate the different series present, and carry out an analytical and property study of the separated hydrocarbons. The sample of Trinidad asphalt was provided by the Barber Asphalt Company, Maurer, New Jersey, and its extraction made possible by a grant from the Warren Fund of the American Academy of Science. The experimental procedure was largely performed at the University of British Columbia, Vancouver, British Columbia, Canada.

PREPARATION OF HYDROCARBONS

Distinctive features associated with the processing of the petrolene hydrocarbons were their extraction from the crude refined asphalt by petroleum ether (b. p. below 50°C.); a high concentration of asphaltic resins during a fuller's earth filtration; a preliminary cutting of the resulting petrolene bitumen into three bulky portions of bituminous oil under carefully regulated vacuum conditions; the application of a solvent dilution process in rapidly acid refining bitumen cuts otherwise too viscous to lend themselves readily to acid processing; the omission of the customary alkali washing treatment following acid refining, and water washing in one instance; digestion of the refined oils over metallic sodium, and their simple bulk vacuum distillation (not fractional separation) twice, over an efficient and simple fractionating column similar to that employed by the U. S. Bureau of Standards[5]; the special investigation of a residual bitumen; the separation of petroleum resins in appreciable quantity, and tar compounds, during acid refining of the heavy residual bitumen; the separation of paraffin wax upon a number of different occasions at approximately 260°C. in vacuo; and a phosphorescent vapor phenomenon.

FRACTIONATION

The above summarized procedure prepared four separate bulky portions of oil, three of them permanently water-white, and estimated in all to consist of approximately 12 percent of the original crude asphalt sample[18]. On one basis the value of 31 percent has been given for the total oily constituents present in Trinidad asphalt[9], whereas on another basis (I, p. 758) the value has been set at 17 to 19 percent (figured on the crude dry substance containing mineral ingredients). This aspect has not been further investigated or confirmed in the present work.

The oils were finally separated in general, into the smallest possible practically constant boiling fractions necessary for a later property and analytical study, through the medium of a single fractional distillation at a reduced pressure of less than one millimeter of mercury, over metallic sodium. In this respect it was the intention to provide the most efficient fractionation possible throughout from a mixture of highly refined water-white hydrocarbons, with lower boiling points secured at a comparatively uniform and constant pressure, and without the irregular boiling and temperature fluctuations accompanying momentary elevations or reductions in pressure. A complete illustrated description of the fractionation apparatus and its operation has previously been outlined (7, p. 53). At this point it suffices to mention that 25 fractionations ready for property and analytical study were secured. As in the case of preparing the water-white hydrocarbons in bulk, during the

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fractionation operation paraffin wax again separated as the distillation temperature approached 260°C., and a re-occurrence of the above mentioned phosphorescent vapor phenomenon took place. Slight but noticeable decomposition also occurred in connection with the last two fractionations, which distilled at over 240°C.

The separation of paraffin wax from a native asphalt forms a very interesting topic of discussion. Accordingly, its separation, various characteristics of the fractionations obtained, and a table of data including unsaturation tests, have been discussed at some length (7, p. 64). The omission of sulfur and nitrogen determinations was considered justified, both because of the methods of procedure of preparation of the water-white hydrocarbons in bulk, and the results of the detailed property and analytical study which followed the fractionation of the bulk oils.

SOLVENT EXTRACTION

Referring back to the original extraction of the asphalt by petroleum ether, it appears evident that for some commercial purposes a more elevated boiling point for this natural petroleum solvent would no doubt prove satisfactory, although similar hydrocarbons have previously been extracted from an Alberta maltha by sulfur dioxide[9], and more recently the petrolene hydrocarbons of a Mexican asphalt by a variety of solvents[21]. In support of the use of the former solvent, water-white hydrocarbons boiling stably to approximately 260°C. followed the solvent dilution for acid refining, of a heavy residual bitumen in a solvent of petroleum ether and acid-treated colorless gasoline, mixed half and half, this procedure permitting a thorough and rapid treatment of the exceedingly viscous and sticky mass. Without doubt varying mixed dilutions of those natural solvents will permit the extraction from such bituminous substances as asphalts, of large proportions of the petrolene hydrocarbons, the blending of the solvents or its combined boiling point as an entity depending upon the boiling point range of the petrolene hydrocarbons desired free from solvent contamination, preferably under vacuum conditions to ensure complete removal of the solvent, and upon the nature of available by-products. This serves to some extent to offset the difficult factors of solvent evaporation and recovery which rendered prohibitive in earlier days the commercial extraction of asphalts by petroleum ether.

The solvent power of petroleum ether upon asphalts has been found superior to that of a number of different solvents, although comparisons with a number of more recently developed commercial solvents are not at present available in print. Earlier work in the field has shown that the sulfur content of the naphtha-soluble bitumen from Trinidad asphalt has been reduced by a marked percentage from that of the entire bitumen, and since a distillation residuum further largely accounts for the elimination of free oil-soluble sulfur, which is practically not attacked by concentrated sulfuric acid, in instances of the present work where extracted oily hydrocarbons were distilled, the application of distillation in vacuo from an ordinary reflux flask served quite effectively in eliminating from distillates most of the sulfur content prior to acid refining processes and digestion over metallic sodium. This was well indicated in part by a pale greenish-yellow colored viscous distillate of high boiling point derived from a special investigation of the residual bitumen referred to above. The sulfur content of the "entire" bitumen of Trinidad Lake asphalt is over 6 percent.

Associated with the preliminary cutting of the extracted and filtered petrolene bitumen referred to above, into 3 bulky portions of bituminous oil, it will be observed that largely similar refining methods have previously been put to use in connection with highly refined oils derived from petroleums, providing, in addition, data on the separation of paraffin wax from refined Trinidad asphalt[2], and they may also be satisfactorily applied in vacuo over efficient fractionating columns together with the extraction and solvent dilution of asphaltic petrolene components by a variety of solvents, possibly avoiding a high loss of oil.

RAPID ACID REFINING

The application of a solvent dilution process in rapidly acid refining bitumen cuts proved to be very satisfactory indeed, the acid refined opaque light colored bulk oils distilling easily in practically all instances to a permanent water-white condition, and eight different factors contributing to the success of the process have been outlined (7, p. 34).

From the reactive viewpoint, the refining action of the concentrated sulfuric acid used was considered very largely a selective one, involving room temperature, acid concentration, the solvent dilution of heavy oil, and time of contact, and it is concluded that the fractionated water-white hydrocarbons were not appreciably acid attacked, if at all, especially since under ordinary refining conditions involving comparatively long periods of contact with sulfuric acid, both paraffinic and naphthenic hydrocarbons remain comparatively inert in reaction. Naphthenes and polynaphthenes were the type of hydrocarbons identified in the Trinidad bitumen through the property and analytical study of the above-referred-to 25 fractionations. However, some of the lower members of the terpene series react slowly with sulfuric acid, and in reference to unsaturation and odor tests of the lower boiling Trinidad fractions (7, p.66), it is quite possible that a slow oxidation reaction, or autoxidation, has been initiated by acid contact with traces of terpenes present, the reaction progressing slowly and more noticeably upon exposure to air and sunlight. Evidently, from the later combustion analyses and related data, sulfonation of the higher boiling fractions had not occurred appreciably, though it is possible that the slight removal of some hydrogen from the stable molecule (dehydrogenation) may have taken place through reduction by metallic sodium, which, it is well to recall, influences a polymerization reaction rather than one of depolymerization. The densities and viscosities of the Trinidad fractionations might have been expected to be increased by refining, but the densities derived in the present work (7, p. 85) are lower in general than those earlier determined by Richardson[18]. A rapid formation of tar compounds during the acid refining of the "residual" Trinidad bitumen, together with a perceptible rise in temperature of the mixture, and the liberation of small quantities of sulfur dioxide gas, strongly implied the presence in the bitumen of very reactive diolefins, and particularly those containing conjugated double bonds.

In correlating the property and analytical data obtained in the present work with that of Krieble and Seyer[9] obtained in connection with an Alberta

maltha, in which similar hydrocarbons were identified, it is definitely concluded that the hydrocarbons identified in the petrolene bitumen of Trinidad Lake asphalt are not the polymerized or depolymerized products of original asphaltic hydrocarbons, although it is to be observed that Richardson[18] has defined malthas as being less susceptible to the attack of concentrated sulfuric acid than are asphalts. The statement, however, obviously holds for the unstable and reactive components of the two different bitumens, rather than the stable processed petrolene naphthene and polynaphthene hydrocarbons, which, in the case of the maltha, were largely prepared water-white by an acceptedly non-drastic sulfur dioxide treatment. It is apparent then, from both the refining proper and reactive standpoints, that the sulfuric acid refining method of this report could have been applied even more satisfactorily to the Alberta maltha than to Trinidad Lake asphalt, and that in the latter case the value of applying the sulfur dioxide process, or others, is further evident, in so far as that reagent competes satisfactorily with the acid when large quantities of the latter are required.

DISTILLATION OF ASPHALTIC OILS

Under different distillation pressure conditions, and using earlier methods at the time, Thiele[20] found it necessary to distil asphaltic oils with great care and with a very gradual rise in temperature, in order to not cause terpene-like decomposition in the distillates of bodies resembling aromatic hydrocarbons, which tend to keep oil yellow in spite of very excellent refining treatment. In the present work on Trinidad asphalt, acid refined and vacuum distilled yellow oils were satisfactorily digested and fairly rapidly distilled to a permanently water-white, non-fluorescent, and odorless condition over metallic sodium, and while colorless oil distilling over sodium may become slightly yellow due to previously incomplete acid purification from contamination, no difficulty of this nature was permanently encountered by the author.

Because of its heavy bituminous nature it was decided to further investigate the distillation possibilities of a small portion of the "residual" bitumen, which eventually yielded oily hydrocarbons boiling above 185°C. at less than one millimeter of mercury pressure. The results have been discussed in some detail (7, p. 35), but because of restricted space here it suffices to mention in this connection, among a few additional observations or conclusions, that as sodium digestion progressed, acid refining having been omitted, the fluid oil turned quite black, with the formation of considerable coke, the black oil in part indicating the presence of decomposing paraffin wax[15]. The latter separated as a waxy deposit on the flask walls especially shortly before the temperature of 260°C. was reached, but a definite cloud point was not observable. The viscous light-colored distillate was quickly refined to a water-white and nearly odorless condition, and this was followed by its individual fractionation to a lowest boiling point of slightly over 185°C. before the high boiling accepted fractionation was further fractionated. A small portion of the oil boiling below 185° was permanently rejected.

Although when an oil is cracked some permanent gas is always formed, during the above special investigation fogging, when it occurred, appeared to be somewhat transient in nature, and by removal and further application of the flask heat it could be avoided for satisfactorily long intervals during a largely uniform temperature rise marked by no pronounced receding. Coincident with the sodium digestion a quantity of gaseous products were evolved, but following this, distillation in vacuo took place more or less uninterruptedly until pronounced fogging commenced at temperatures unascertained below 260°C. A very rapid temperature rise to 320°C. accounted for very little distillate from the small bitumen sample being distilled, reflux distillation at slightly over 260°C. dropping off quickly. That no greatly marked receding or uncontrollable fluctuation of the distillation temperature was observed further strengthened the evidence that very little decomposition or alteration was associated with the actual hydrocarbons distilling over in vacuo. The light color of the entire distillate was particularly satisfactory, and this emphasized the value of distillation in vacuo of heavier bitumen sulfur oils to avoid considerable loss in acid refining. Gaseous products and the occurrence of fogging were evidently largely associated with the evolution and decomposition of extraneous and non-volatile bituminous matter, more so than with the "vacuum distilled" petrolene hydrocarbons. According to Abraham[1] a soft pure Hungarian asphalt proper has been distilled to recover the heavy oils, and even gilsonite may be distilled until the vapors reach a temperature of 550°F. (288°C.), following which an exothermic reaction takes place and the evolution of gaseous products becomes exceedingly rapid. Abraham has further observed that upon heating bitumens at atmospheric pressure they commence to distill without decomposition, and in consideration of the observations and experimental data recently compiled[7] it is concluded that vacuum distillation at the temperatures specified neither polymerized or depolymerized any of the 25 water-white fractionations obtained, and that the highest boiling fractions did not include polymerized or depolymerized hydrocarbons introduced from a more or less non-volatile residual bitumen. It is considered that commercially refined asphalts, free from moisture, can eventually be distilled at satisfactorily reduced pressures at least to a certain extent without the decomposition of stable petrolene hydrocarbons, although much coking and decomposition may occur at the same time to contaminate distillates, and though it be obviously necessary to distribute heat quite evenly throughout stills by such devices as the steam coils already in use.

SEPARATION OF PARAFFIN WAX

The separation of paraffin wax from Trinidad asphalt, though not a new observation, is of considerable interest. Associated with sulfur dioxide refining Browery[3] at —12°C. secured a highly satisfactory separation of about equal parts of aromatic and paraffin hydrocarbons from the light distillate of a Trinidad crude petroleum boiling up to 150°C. The comparative findings are interesting, therefore, both because of the proximity of the fields, and because no liquid paraffins were recovered in the present work from Trinidad asphalt. Because of a frequent property similarity of paraffin hydrocarbons to naphthenes, it is expected that a more detailed analysis of the supposedly paraffin hydrocarbon extraction, which was beyond the scope of Browery's work, would have proved the hydrocarbons to be of the naphthenic type.

It is interesting to note that while data compiled by Abraham (I, pp. 102, 135) account for the presence of no solid paraffin wax in refined Bermudez and Trinidad native asphalt, on the other hand Allen,

Jacobs, Crossfield, and Matthews[2] have separated as much as over 10 percent of wax from refined Trinidad asphalt. Abraham has pointed out further, however, that solid paraffin wax has been identified in asphalt from Matitza, Rumania and Japan; in gilsonite, grahamite, and glance pitch; residual oils and asphalts; and sludge and blown petroleum asphalts. Since paraffin wax apparently did not separate from the maltha extraction of Krieble and Seyer[9], it is very possible that it would have done so under the same conditions specified in the present work, and a similar possibility holds for native Bermudez asphalt. At this point then, it is important to observe that the presence of solid paraffins does not serve to distinguish residual from native asphalts, since both may contain them.

PHYSICAL PROPERTY AND ANALYTICAL STUDY

The study of samples of crude oil have shown that physical and chemical properties may vary with the depth of production[8], and it is evident that such variations may largely be associated with the factors of source of origin, geological influences and environment, and a gradual geological metamorphosis of the ingredients. On the other hand, in view of the comparatively uniform composition of surface Trinidad Lake asphalt, it is expected that the identification data determined in the present investigation (7, Table 1) will hold more or less in general for any sample (taking the size of the sample into consideration) of that particular asphalt "commercially refined" under similar conditions, or specifications.

In respect to the property and analytical study of the 25 Trinidad fractionations referred to above, density determinations of the individual fractions were carried out immediately following their fractional distillation. Then followed measurements of their refractive indices, viscosities at 20°C., the combustion analyses, molecular weight determinations, viscosities in ten degree intervals from 20° to 100°C., optical rotations, and finally unsaturation tests and a two weeks exposure of the 7 lowest boiling fractions to the atmosphere and sunlight. The data obtained, including estimations of molecular refractions and volumes, have all been recently compiled and additionally illustrated by graphs (7, Tables 1 and 2).

DENSITY AND REFRACTIVE INDEX

The density determinations were made at 20°C. using an ordinary pycnometer and the same water bath as that by which the indices of refraction were obtained at the same temperature. A decreasing density relationship in respect to the refined bitumen pointed to the efficiency of the purification or refining processes, and together with a normal increase in the combustion carbon-hydrogen ratios strongly implied that the sulfuric acid and related refining methods employed were not appreciably drastic in action. The comparatively low density data pointed out the absence of polymerization and depolymerization during the preparation of the hydrocarbons for study, and it is interesting to note in this connection, that McKee[14] has outlined somewhat similar specific gravity data for crude fractions derived also "in vacuo" from Scottish and Utah shale oils. This rough similarity is obviously important in so far as the distillation of shale oils is in general termed a destructive one, whereas considerable precaution has been taken in connection with the present work to not permit an appreciable attack of the naphthenic hydrocarbons studied.

An interesting inter-property and analytical relationship existing among fractions 15 to 19 was found, for which the densities indices of refraction, and hydrogen combustion data gradually decreased with the boiling point rise, while the viscosities, optical rotations, and molecular weights gradually increased. The relationship was further interestingly represented by graphical curves of the data involved. The absence or presence in only small quantity of the hydrocarbon $C_{23}H_{42}$ seemed undoubtedly partly responsible for the unusual inter-property relationship. Large increments in the densities and indices of refraction from fractions 20 to 25 were indications that a more extensive extraction of Trinidad asphalt than that of the present work might have lead to the identification of additional hydrocarbons. The indices of refraction were determined with a Pulfrich refractometer set for this work, using the sodium line, and all density and indices measurements were very carefully checked.

VISCOSITY AND OPTICAL ACTIVITY

It has been concluded by Riehm[19] that the influence of paraffin wax on the properties of asphaltic bitumen is to lower the asphalt's viscosity and adhesiveness. But whereas viscosity measurements made by the author did not include the presence of paraffin wax, the involved effects have not been ascertained in the present work. All viscosity data at 20°C. were determined and carefully checked using an Ostwald viscometer before additional data at other temperatures were found. In reference to the viscosity curves of the fractions at temperatures from 20° to 100°C., curves for the first seven fractionations, representing all of the C_nH_{2n-2} series hydrocarbons identified except $C_{18}H_{34}$, were found to rise nearly vertically throughout the entire temperature range noted above, for periods of efflux not very widely divergent, of around 1000 clock seconds at 20°. An interesting observation followed, of the approach of the curves of the first 20 fractions from widely divergent viscosities of 388 seconds for fraction 1 and well over 24,000 clock seconds for fraction 20, at 20°, to periods of flow all grouped closely below 750 seconds at 100°. The curves for the last five fractions all represented high changeable viscosities, illustrating as well the increasing effect of plasticity.

The optical activity measurements were performed on polarimeter No. 28242, (Adam Hilgar, London), the curve resulting at 20° corresponding more with that of the viscosity measurements at the same temperature than with any of the other property curves.

MOLECULAR WEIGHT

The molecular weight determinations were made by the freezing-point method using benzene as the solvent, and the simple modification of a platinum wire method devised by Maass[11], which has been fully discussed (7, p. 104). Since some difficulty was experienced in securing the best crystallization with the platinum wire method, and since, for example, hydrocarbons of the aromatic series do not crystallize easily, it is quite probable that beside the possibility of faulty construction by the author of the platinum wire apparatus, the method must also allow for some variability in the ease of initiating crystal formation. The modified method was based upon the principle of maintaining one or a very few crystals

present at a temperature of about one degree above the true freezing-point previously to new readings. Seeding was therefor not necessary.

COMBUSTION ANALYSES

Duplicate combustion analyses both with and without lead chromate for the detection of sulfur, were performed using all the precautions necessary with experience in this kind of work[12], and data showing the total carbon and hydrogen percentages illustrated the efficiency and completeness of the combustions, in part the freedom of the oils from sulfur and nitrogen impurities, and from oxygen compounds, and paraffin wax. By comparison with other bitumens an increase of the carbon and "hydrogen" percentages with superior refining became apparent, and "atomic" carbon and hydrogen data justified the identification of 18 individual hydrocarbons and hence their corresponding hydrocarbon series, namely, the C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-6}, C_nH_{2n-8}, and C_nH_{2n-10} series, although in connection with the last series mentioned it will be realized, of course, that a very slight experimental error indeed, of less than one half percent in molecular weight determinations, may mean the difference between a lone hydrocarbon representing the C_nH_{2n-8} and the C_nH_{2n-10} series. Because of the one lone representative hydrocarbon identified, absolute conclusiveness as to the presence of the latter series is not yet considered fully established. Solid paraffin wax was representative of the paraffin series, and a decreasing terpene-like odor of the first five fractions together with an initial molecular weight of 185 for fraction 1 all formed evidence in part for the presence of the terpene series as a trace in the commercially refined sample of Trinidad Lake asphalt. Terpenes have been identified in gilsonite and grahamite[13], and also in the Alberta maltha previously mentioned[9].

MOLECULAR REFRACTION AND VOLUME

Molecular refraction determinations partly served to illustrate the extent of separation of individual hydrocarbons during fractional distillation, and further proved the purity of the fractionated oils from foreign contamination.

Molecular volume estimations clearly proved a cyclic or ring structure for all of the identified hydrocarbons, and provided decisive evidence to support the conclusion in part, of Richardson[18], that all of the hydrocarbons of asphalts are of the unsaturated type.

CONCLUSION

In closing it is fitting to refer to the conclusion of Leslie[10] to the effect that there is much to be learned about the chemistry and physical properties of the naphthenic class of compounds, which resemble the paraffins in their chemical inertness, but which can be more or less readily dehydrogenated to aromatic hydrocarbons with quite different properties. According to a newer classification of petroleum by Kraemar and Garton[8], characteristics of the Trinidad petrolene bitumen indicate it to be of an intermediate base because of the separation of paraffin wax, whereas high density data suggest a naphthene-intermediate base[10]. According to the present work done on Trinidad Lake asphalt it seems more accurate to define the base of the substance with reference to the fairly detailed work performed on the extracted bitumen, rather than from the residual original crude asphalt itself, that is to say, on the basis of an asphalt being a highly residual form of petroleum.

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A New High Octane Blending Agent

(*Continued from page 305*)

to meet special requirements. In cases where higher front-end volatility is desired, a material such as iso-pentane can be used without any material sacrifice in anti-knock value.

MULTI-CYLINDER TESTS

Tests have been run on high output multi-cylinder engines comparing the performance of the following fuels:

Straight-run gasoline + iso-octane + lead	to 100 O.N.
Straight-run gasoline + isopropyl ether + lead	to 100 O.N.
Straight-run gasoline + lead	to 92 O.N.

Conclusions drawn so far indicate:

1. The 100 O.N. isopropyl ether blend has a minimum specific fuel consumption 13 percent lower than the 92 O.N. regular gasoline when run under cruising conditions.

2. The 100 O.N. isopropyl ether blend has a minimum specific fuel consumption 5 to 7 percent higher than the 100 O.N. iso-octane blend under cruising conditions. This is in proportion to its lower heat content.

3. The lower economy of isopropyl ether may be overcome by going above 100 O.N. which is possible with this material.

4. The 100 O.N. blends of isopropyl ether and iso-octane are equal in power output and consumption under high power conditions such as used during take-off.

Jets and Mixers

Reduce Costs of Treating

J. C. ALBRIGHT

M. F. WILCOX OIL & GAS COMPANY has been using doctor solution (sodium plumbite) to treat all products made in its refinery which can be used for motor fuel since acid treatment was discarded some time ago. The solution used for treating straight-run, vapor-recovery and cracked gasoline from the Dubbs unit is mixed in much the same way that is used by refiners generally. However, to prevent accidents due to caustic burns, the company has covered the mixing vats with a mesh of rods, welded together to form a platform upon which an employee may walk, but large enough that water and caustic solution can readily fall through to the vats below.

The caustic used comes in the usual drums, and when reducing it from the solidified state to a liquid, a row of drums is placed upon the mesh cover where a manifold of steam pipes is arranged so a number of drums can be reduced at one time. A stream of air is used to agitate the caustic mixture as it is being prepared and while the litharge is being added.

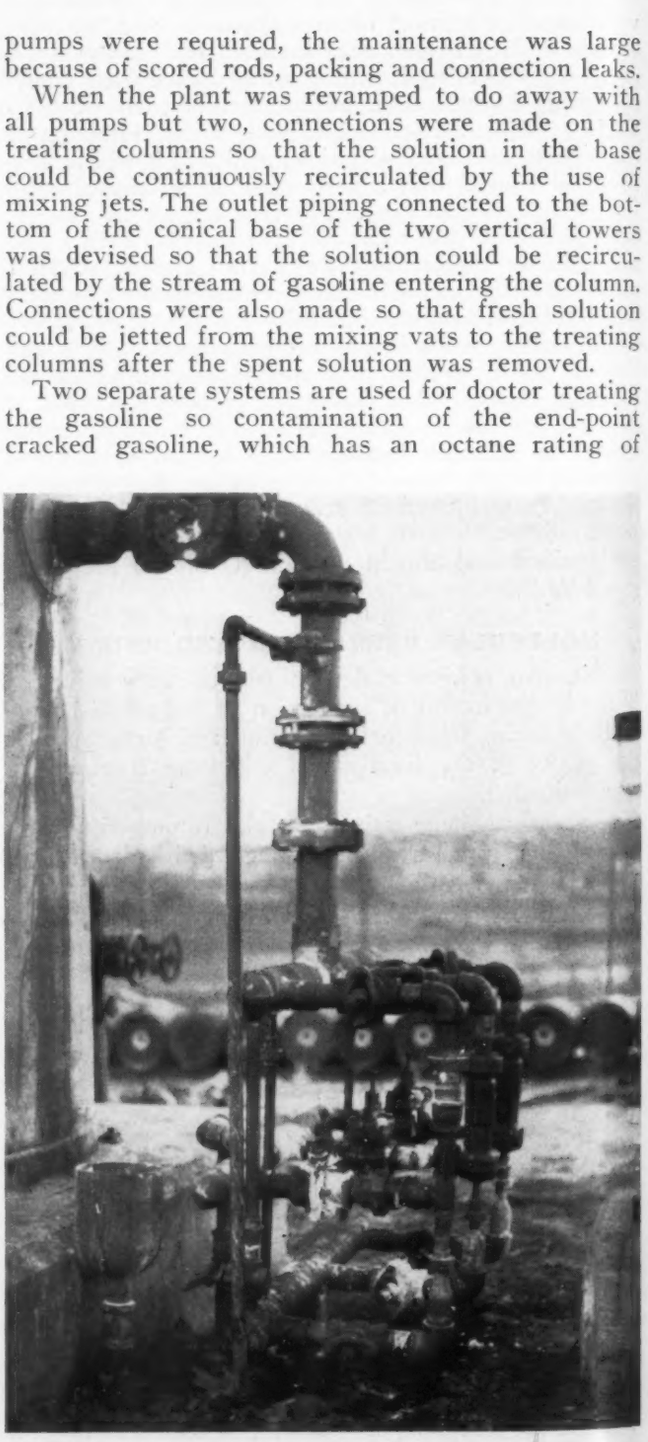
The treating columns have been used by the company for several years, and are about 30 feet in height and about 5 feet in diameter. The lower ring of these vertical vessels forms a skirt in which the conical base is contained, and where the draw-off connections are placed.

During former operation of the doctor plant, several pumps were used to circulate the gasoline, the doctor, and to draw off the spent solution and fill with fresh after the treating agent had become weakened. Since the plant has been redesigned, only two pumps are used, and these handle the gasolines being treated. Two separate systems are grouped together, one for straight-run and vapor-recovery gasoline, and the other for cracked gasoline after the pressure distillate has been rerun for end-point and other specifications.

The first phase of the treating begins at the vapor condensers where caustic is introduced to remove the sulfur compounds, particularly hydrogen sulfide, and also to retard corrosion in the vapor system of the distillation units. This operator has found, like other refiners, that a pre-caustic contact provides a longer life for the doctor solution and makes for better all-around treating. Introducing the caustic in the vapor lines does not require contact columns or other devices and also does not require large pumps to handle the solution. Further, when several pumps were required, the maintenance was large because of scored rods, packing and connection leaks.

When the plant was revamped to do away with all pumps but two, connections were made on the treating columns so that the solution in the base could be continuously recirculated by the use of mixing jets. The outlet piping connected to the bottom of the conical base of the two vertical towers was devised so that the solution could be recirculated by the stream of gasoline entering the column. Connections were also made so that fresh solution could be jetted from the mixing vats to the treating columns after the spent solution was removed.

Two separate systems are used for doctor treating the gasoline so contamination of the end-point cracked gasoline, which has an octane rating of



Manifold arrangement of treating compound jets used in pressure distillate-treating column.

around 71, could be prevented by using only one of the columns for this liquid, and the other vessel for straight-run and vapor-recovery gasoline. Vapor-recovery gasoline, made from the cracked pressure distillate vapors at the stabilizer plant, also is given a pre-caustic wash in a separate tank before it is treated with doctor. This is accomplished through the use of system pressure forcing the gasoline to a horizontal storage tank which is also fitted with a jet mixer and recirculates caustic in the bottom of the tank with the fresh gasoline forced to it from the vapor-recovery accumulator drum.

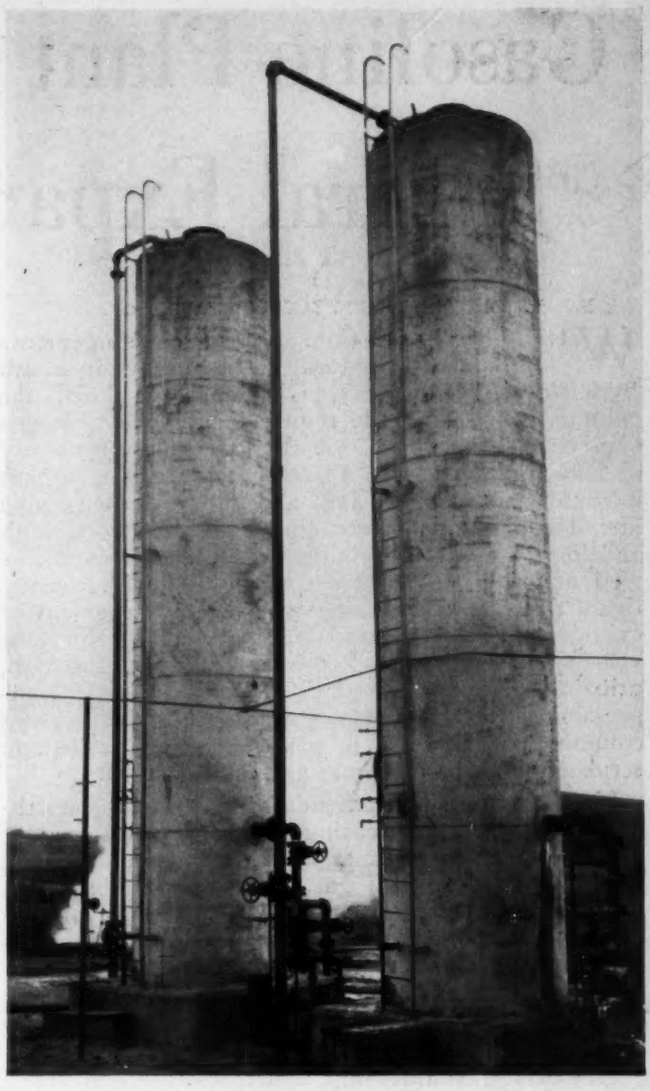
The tank is filled to about 18 inches with caustic solution having a Beaume gravity of about 25 degrees. Connections are placed in the tank so gasoline can be removed by pressure without taking any of the caustic solution with it. An internal nipple is connected to the tank drain flange which extends upward for about 2 feet, well above the caustic level in the tank. The inlet connection of this tank is fitted with a jet which takes caustic from the bottom of the shell and thoroughly mixes it with the gasoline as it enters the shell of the tank through this mixer.

When the cracked gasoline is ready for treatment it is pumped from run-down tanks with a reciprocating steam pump and forced through a line leading to the "Christmas tree" connections at the treating column. This "Christmas tree" contains three jets, any multiple of which may be used, depending upon the amount treated and the velocity of the liquid entering the column. A riser attached to the top of this bank of jets contains additional mixing devices. The line leading from the riser extends into the tank and upward about 3 feet above the level of the doctor solution. The top of this riser is fitted with a tee, bullheaded, to which is connected two ells, looking downward to throw the gasoline and doctor to the bottom of the tank for better separation before the gasoline leaves the tank.

When fresh solution is needed, the line leading from the mixing tanks, or vats, is opened and the jets pull the fresh doctor to the treating column until the correct amount has been added. Gasoline is always in contact with doctor while flowing into the column, either when regular treating is being conducted, or when fresh solution is being added, or the column filled with fresh treating solution.

The straight-run column is fitted with a similar connection and operates in the same manner. This column is used for both the straight-run and vapor-recovery material. Only one pump is needed for this purpose, and to overcome what gas lock might occur while handling the 26/70 grade of vapor-recovery gasoline, pressure is placed upon the horizontal tank to provide a pressure on the suction of the treating pump while handling this material.

The sulfur pots were placed apart from the treating columns, and near the chemical storehouse for convenience in loading with stick sulfur when the previous charge is used. These pots were made by using 20-inch casing with a welded bottom and a bottleneck top. They were placed upon concrete piers by attaching pieces of angle iron to each side for rests. The bottleneck tops are fitted with flanges for a cover, the removable flange being closed with a short flat plug having a bail welded to it so the operator can remove it without difficulty. Each of these pots were fitted with "Christmas tree" inlet



Treating plant, H. F. Wilcox Oil & Gas Company, Bristow, Oklahoma. Columns on right is used for treating pressure distillate; column on left handles straight run and recovery-plant gasoline.

connections to control the amount of gasoline passing through the bed of sulfur.

The pump pressure on the main stream of gasoline forces the split stream through the sulfur pots and the sulfurized gasoline enters the treating device between the two mixers placed in the riser above the circulating jets at the vertical columns.

After the gasoline has been contacted with doctor in the "Christmas tree" fittings and the vertical riser at the columns, it is continuously vented from a connection placed in the top head of the columns, the line turns and follows the line of the columns to the ground and to storage. But in this line, connections were also made to introduce water for washing the gasoline after it has been treated. A mixing device was placed in the line through which both the water and treated gasoline must pass. The water is metered to the line to prevent the use of an undue amount, and the gasoline and the water both travel through the line to storage. These tanks act both as storage for treated gasoline and as water settlers. When the water separated from the treated gasoline, an inhibitor is used with the cracked stock to prevent the formation of objectionable gums.

Gasoline Plant Passed Through Several Expansion Programs

WHEN Skelly Oil Company made arrangements to construct a natural gasoline plant in South Burbank, Osage County, Oklahoma, in 1934, the volume of gas available required only five twin gas engine-driven compressors. Because of the necessity of boosting the gas to a pressure high enough that it could be introduced into a common carrier's pipe line, these engines were equipped with both high and low compressor cylinders. Before the plant was well under way it was necessary to add five additional engines of the same type and arrangement of cylinders. Gasoline was obtained during the first year by the use of high pressure gas fractionation, utilizing the pressure of the second stage of compression to introduce the gas into the fractionating column, from which it passed through adequate scrubbers into the pipe lines and residue systems.

Since the field was extended rapidly to the northeast with an ever increasing supply of gas, the plant was increased in capacity again in July of 1935. At this time, a supply of gas became available which made it possible to operate a low pressure oil absorption plant on the same site with the high pressure gas fractionation unit. The volume of gas, both high pressure and low pressure, became so great that it was again necessary to enlarge the compressor capacity by adding three twin, four-cycle gas engine-driven compressors, which was done at about the same time that the low pressure oil absorption unit was placed in operation.

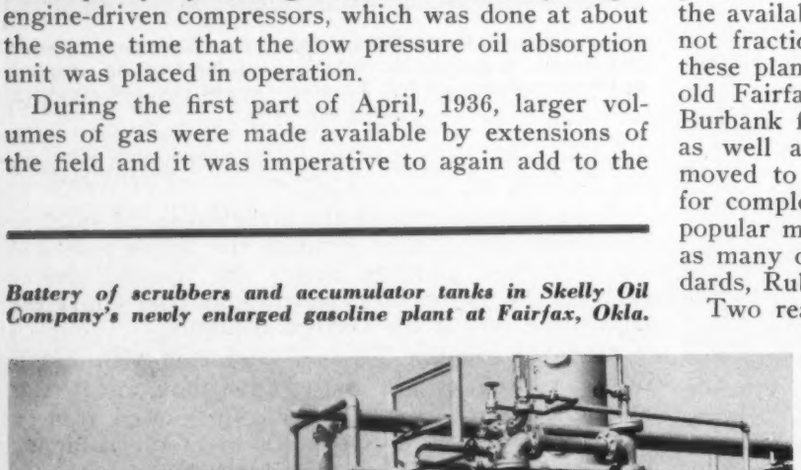
During the first part of April, 1936, larger volumes of gas were made available by extensions of the field and it was imperative to again add to the capacity of the plant. Two more of the four-cycle gas engines were installed. These did not relieve the situation to any great extent, because of an increased supply of gas made available at the time the new engines were set. About three million cubic feet of the gas from the north end of the field was piped to "Carter Nine," a plant operated by Skelly Oil Company in the old Burbank field, but with this amount removed from the field, an additional 10,000,000 cubic feet remained to be processed.

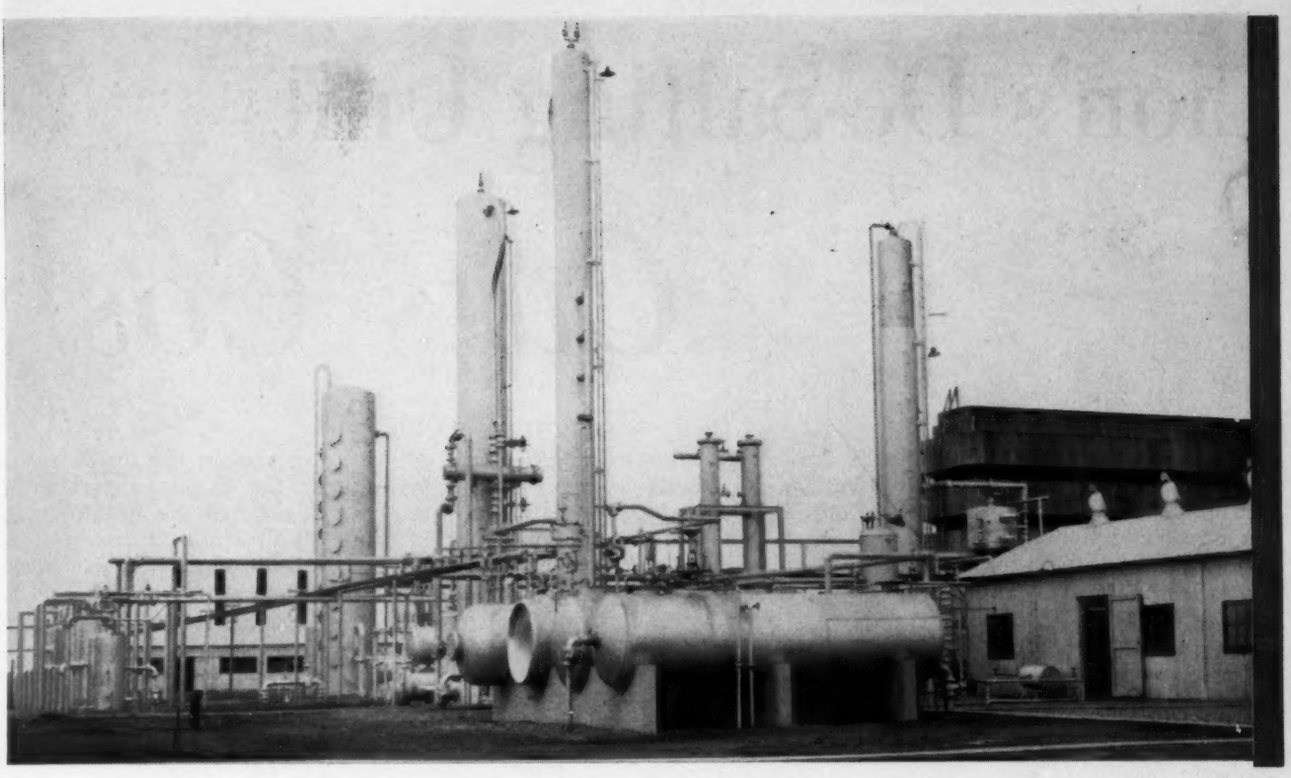
As a result, a new plant was built in the section north of the Fairfax plant, which contains 10 twin two-cycle gas engine-driven compressors. This plant operates on the first stage of compression—about 50 pounds—using oil absorption to recover the gasoline. Both high and low pressure cylinders are used on these 10 engines, the low to bring the gas from the traps and separators and pass it through the absorption unit. The high pressure cylinders pick up the residue and boost it to 275 or 300 pounds at which pressure it is pumped into the transmission lines of the local gas company, or picked up by a production booster station and returned to the gas cap of the producing structure for pressure maintenance on the sands.

Gasoline manufactured at both the old Fairfax plant and the new one is made so it will contain all the available propane and butanes in the gas and is not fractionated for recovery or vapor pressure at these plants. A pipe line was constructed from the old Fairfax plant and extending through the Old Burbank field, where gasoline made at Carter Nine as well as that made in South Burbank can be moved to the company's Lyman, Oklahoma, plant for complete fractionation. Stabilized natural of the popular market grades are made at Lyman, as well as many different specialties, such as VM&P, Stoddards, Rubber Solvents, and USP naphthas.

Two reasons are given for the necessity of two-staging the gas in the field. First, because of an agreement among the producers that low pressure must be maintained upon the field oil and gas separator outlets, and secondly, gas handled under high pressure leaving the traps and separators would leave a great part of the desirable hydrocarbons dissolved in the crude, which, upon being pumped to tank batteries would be lost. Even when gas is handled in this manner, the gasoline content varies greatly, showing on physical tests a content from 0.1 gallon per thousand cubic feet to as high as 2 gallons per thousand cubic feet, with the average about 1.25 gallons of raw gasoline. When fractionated, or stabilized, to a marketable product, the

Battery of scrubbers and accumulator tanks in Skelly Oil Company's newly enlarged gasoline plant at Fairfax, Okla.





Gas fractionation and low pressure absorption units in Skelly Oil Company's Fairfax gasoline plant in South Burbank field, Osage County, Oklahoma.

average is about one gallon per thousand cubic feet.

The layout of the plant was made so all pumps of the same classification could be placed in a common building, such as absorption-oil, gasoline and reflux pumps together, and, water for cooling-tower service and engine-jacket water in another. The pumps used for oil and gasoline circulation and handling are all steam-driven reciprocating units while water pumps are all centrifugal, with the service units pulled from a common line shaft. The shaft is at proper height that operators encounter no difficulty in running a belt upon the driving pulleys when standing upon the floor. The steam-driven oil and gasoline pumps are spaced wide and upon high blocks to make it more convenient for mechanics to repack and accomplish the various duties attendant to upkeep.

Gas, oil and gasoline lines, as well as steam lines are carried above ground, with the exception of raw unprocessed casinghead gas. Some of these lines were insulated to prevent heating from exposure to the sun and hot winds. Efficient cooling is obtained through the use of a modern cooling tower having a minimum of wind loss of water. The tower was expanded to about 30 percent when the low pressure absorption unit was built and uses atmospheric cooling sections.

Standby water pumps have been placed at two different points in the plant, one in the water pump room and another in a building near the cooling tower. Both these emergency pumps are single-stage centrifugal, low-head type, and are driven by automobile motors. The motors were purchased new, and connected directly to the pump shaft without speed increasers. To obtain the maximum efficiency of these pumps, the motors must turn up to about 1750 revolutions per minute when operating. It is not unusual to find automobile motors doing service in the various oil fields over the country, but it is uncommon to find a new eight-cylinder motor purchased especially for this class of work. The motors have been equipped with a standard gas-mixing valve so they can obtain fuel from the plant gas lines. The usual complement of electric generators and starters, together with the storage battery is used as in the original automotive service for which these engines were designed. Cooling is obtained by circulating water through the jackets. The radiator cooling fans were left on these units which circulate sufficient air to prevent overheating of the generator. Governors were installed on these two motors to prevent excessive and destructive speed if and when circulation of water terminates for any reason.

Only 17 days were needed for the construction. Hard rock covers the majority of the country in this part of Osage County, but with foundation pits to be excavated, concrete blocks poured, intake and discharge lines extended and the two 165 horsepower 4-cycle engines grouted in and tuned up, only that short period was necessary. Good planning and crew coordination were responsible for the remarkable speed shown in erecting these engines; each man in each crew had a specific job laid out for completion, and as few men as possible were detailed for the work, thus eliminating much of the overlapping found where large gangs are employed.

The combined processing capacity of the two plants is about 25,000,000 cubic feet of gas. Provisions have been made in the gas headers to take care of further additions without interfering with units in operation.

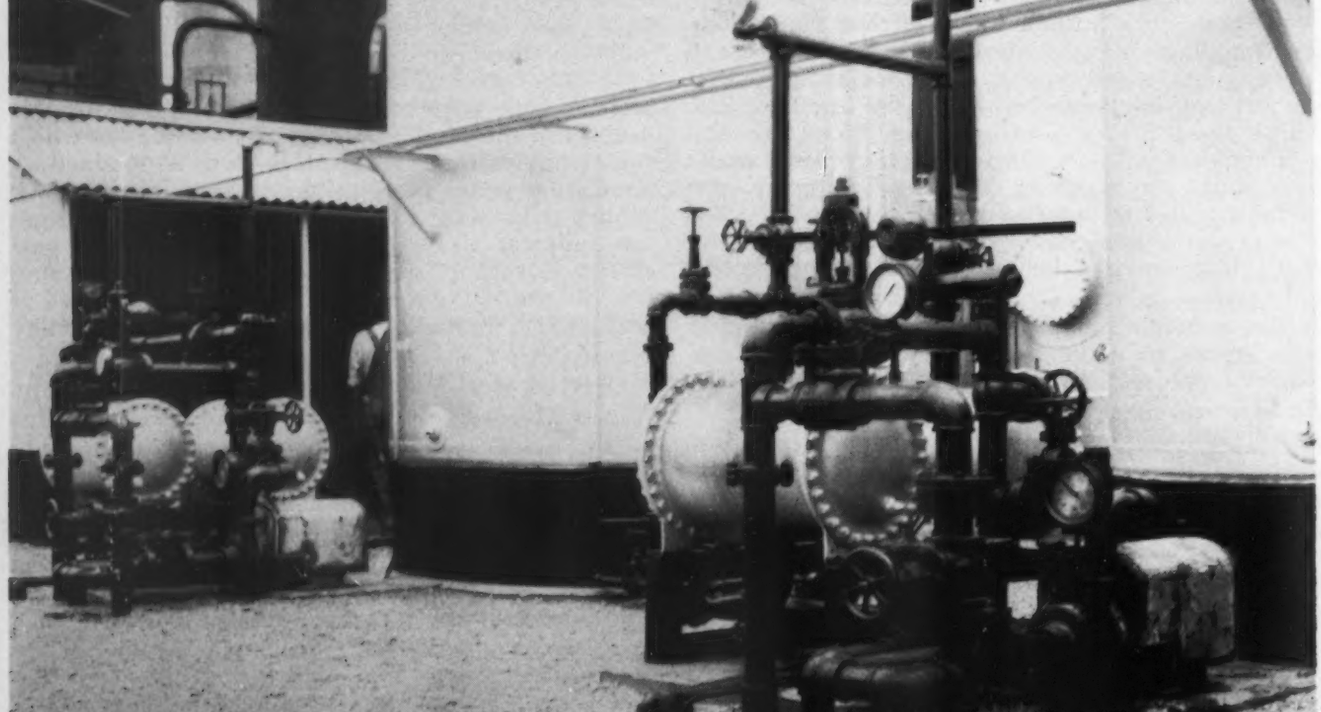
Lion's De-Salting Unit *Cuts Costs*

PROCESSING a heavy Arkansas crude which has about 180 grams of salt per barrel when it is delivered at the refinery, Lion Oil Refining Company has encountered chloride corrosion in various parts of the distillation unit handling this crude. The salt contained in the oil is peculiar in that it is in a crystalline form, instead of as a salt water emulsion. Ordinary methods used to break an emulsion did not accomplish the desired results, due to the fact that each salt crystal is surrounded with a tough film of asphaltic oil which was difficult to break down to permit the treating compounds to reach the crystals. Quantitative analysis disclosed the fact that the crude contained an average of 180 grams per barrel, which was sufficient to cause not only corrosion of the equipment, but to deposit crude salt in exchangers and other parts of the equipment.

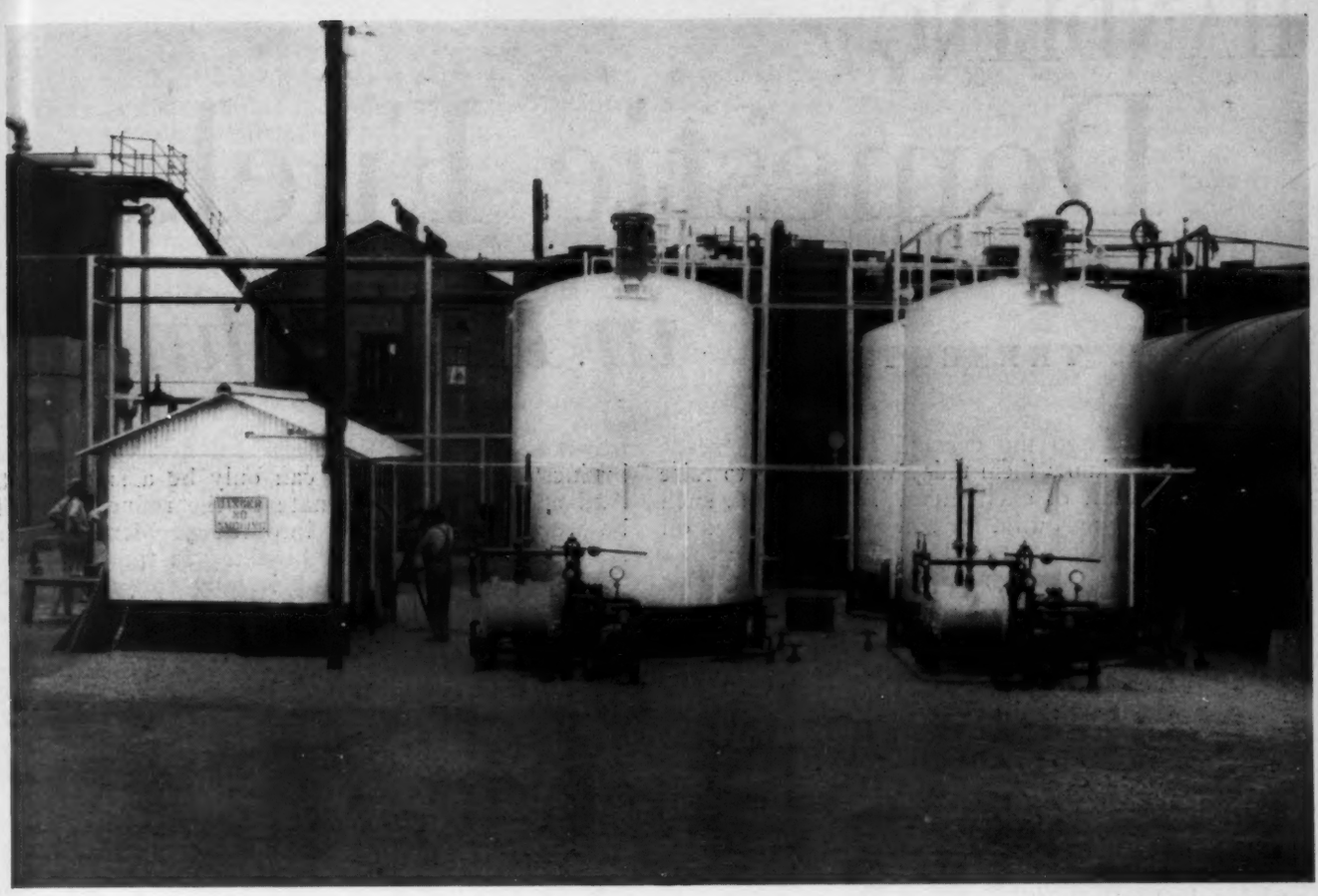
About the first of June, 1936, a new type plant was installed to remove the salt from the crude by electrolysis. The plant is of the same general type as operated by producers in the field for breaking down the emulsion in crude. Test runs on the unit have shown that the salt content was reduced from the average of 180 grams per barrel to as low as 3 grams per barrel on the outlet of the treating units, and at a cost which is not excessive.

Due to the amount of oil processed daily, approximately 2500 barrels, it was considered expedient to install 2 units, each containing 2 treating vessels, connected in such a manner that each unit is operated in parallel with the other. The vessels have a dimension of 10 feet by 12 feet, standard API construction, each pair equipped with heat exchangers, pumps, orifice mixers and back pressure regulators.

The problem here was not one of breaking down an emulsion, but one of creating an emulsion to or-



Apparatus for intimate mixing of oil and hot water so that salt crystals may be disolved and removed.



Petroleum Rectifying Company's desalting unit in refinery of Lion Oil Refining Company at El Dorado, Arkansas.

der, and then breaking that down so that the saline content of the oil could be reduced to a percentage that would not cause excessive corrosion of metallic equipment. In the ordinary sense, an emulsion is considered a mixture of oil and water, with the water dispersed throughout the oil in minute particles, each one surrounded at the point of contact by the agent responsible for the emulsion; the chemical in the oil or water which binds the droplets to the mass in such a manner that they will not settle readily to the bottom of tanks. In this case, water was removed in the field, but not the crystalline salt.

The 19 gravity oil is pumped to the units from the plant working tanks through the desalting heat exchangers, with desalted oil flowing counter current to the fresh charge to a point in the system where the hot water is injected into the stream. Mixing is obtained through three separate devices, the first being two-inch orifices in a six-inch line followed by a motor driven centrifugal pump. The function of the pump is not one of charging the oil and hot water to the units, but to churn the water and oil so that the interfacial bond surrounding the salt crystals can be removed in order that the hot water may dissolve them. The pump is followed by a back-pressure regulator placed in the line to give the stream an additional agitation and rough treatment so that all of the crystals in the oil will be forced to shed the heavy tarry skin.

The water used is a stream coming from the boiler feed pumps with a temperature of about 170°F., and with a volume of approximately 20 percent of the oil. The oil at the point of first contact with the water has a temperature of about 140°F., which with the hot water, places a temperature sufficiently high upon the material passing through the agitating devices that practically all of the salt crystals are dissolved.

The oil and water, forming a made to order emulsion is then directed into the treating vessels for the removal of the water. More or less the same procedure is followed by the flow through the vessels as that practiced with flow line treatment of oil in the field. A predetermined level of water is maintained in each vessel; the emulsion is introduced above that point, and comes in contact with the electrical field which causes the minute droplets of water to coalesce into larger droplets of sufficient size and weight that they separate easily from the oil; water falling to the base of the tank and the oil rising to the outlet.

A calibrated weir box between the two units measures the water removed from the oil, as well as meters on the inlet of the stream of hot water from the boiler feed pumps. The transformers which reduce the electrical current to sufficiently high voltage to operate the units are mounted on bases placed on top of each vessel so that employees may not come in contact with them. The control room, containing the centrifugal pump switches and the indicating instruments connected to the current supply is located near the units for convenience.

HANDLING Domestic Fuels *in the Refinery*

L. C. TRESCOTT

A FEW years ago the demand for light domestic fuels as we know them today was nothing to raise any great amount of excitement. The demand, such as it was, made an outlet for some grades of gas oil at some added profit, but on the whole there was not enough business that anyone gave any particular concern to the means of handling and distributing it, at least so far as the refinery was concerned. There were always fuel oil lines to the tank car loading racks and a stand-pipe of some sort hooked into one of those lines and supplied by the regular fuel oil pump, usually sufficed for loading the few trucks that came in. Very seldom were meters installed and the loads were made to the "finger" in each compartment. No orders for less than single compartments were filled. Usually, too, the local orders were limited to large buildings where the oil was handled in full loads.

With many concerns no particular effort was made to manufacture such fuels. Tanks of gas oil which came within the specifications were set aside. This practice usually kept sufficient stock on hand. Some concerns, to make a grade equal to No. 3 fuel, simply mixed No. 2 and No. 4. The business was taken as it came and handled in the easiest way possible.

In many districts it was the coming of the oil-burning heating stove and the development of burner systems within the reach of the average home that changed all this. Instead of full loads or at least full compartments, deliveries are made ranging from 50 gallons up. Underwriters and other requirements have brought real specifications and the volume of business has grown until it is necessary to give some thought to taking care of it.

In this connection it is interesting to note that in one rural township having two small towns within its borders, well over 60 percent of the houses are already equipped either with oil-burning heating stoves or oil-fired central heaters. This does not include the kerosene heaters but only those using No. 2 fuel or heavier. The above condition is a sign of what may be expected in the line of expansion from this branch of the petroleum industry. It is a condition which has been brought about not because fuel oil is a cheaper or more economical fuel than coal, but because it is cleaner, because of its convenience, because it does give more uniform heating and—this last has contributed in no small measure to the expansion—the dealer takes a real responsibility for its delivery to the consumers' tanks or drums. The up-to-the-minute dealer keeps a check on his customers' tanks. He makes deliveries in any quantity, and at any time, regardless of the weather.

The past year has seen the domestic fuel requirements at least triple themselves. Considering present business conditions, this can only be a small start. And as the stocks originate in the refinery it will be worth while to look into the problem of their manufacture and of their handling at that point.

The smaller bulk station is only concerned with the receipt of the various grades of fuel into its tanks and the delivery to trucks. The refinery is concerned with the manufacture of the fuels; the gathering of the various stocks from various sources and their blending to meet specifications; the drying and preparation of the fuels for shipment, and finally the problem of speedy and efficient delivery to trucks, tank cars or barges.

SPECIFICATIONS

Government specifications are good ones to use as a guide. Most concerns modify these to suit their own stocks and the requirements of their own customers, but they at least furnish a good starting point. Under this head come four grades.

No. 1 Fuel

Gravity—38.0-40.0° A. P. I.
Flash—Minimum 100° F. or legal; maximum 150° F.
Water and Sediment—0.05 percent.
Pour—Maximum 15° F.
Distillation—10 percent 420° F. maximum; endpoint 600° F.
Sulphur—0.5 percent.
Carbon Residue—0.02 percent maximum.
No. 1 fuel is practically a waterwhite distillate. Some concerns ship regular grade kerosene on orders for this fuel.

No. 2 Fuel

Gravity—36.0° A. P. I.
Flash—Minimum 100° F. or legal; maximum 190° F.
Water and Sediment—0.05 percent.
Pour—15° F. maximum.
Distillation—10 percent 440° F.; 90 percent 620° F. maximum; endpoint 600° F. minimum.
Sulphur—0.50 percent.
Carbon Residue—0.05 percent maximum.

No. 3 Fuel

Gravity—33.0° A. P. I.
Flash—Minimum 100° F. or legal; maximum 200° F.
Water and Sediment—0.10 percent.
Pour—15° F. maximum.
Distillation—90 percent* 620° F. minimum.
*This requirement shall be waived when the carbon residue is more than 0.07 and less than 0.15 percent.
Saybolt Viscosity at 100° F.—70 secs. maximum.
Sulphur—0.75 percent maximum.
Carbon Residue—0.15 percent maximum.

No. 4 Fuel

Gravity—31.5° A. P. I.
Flash—Minimum 150° F.
Water and Sediment—1.0 percent.
Saybolt Viscosity at 100—*70 secs. minimum; 500 secs. maximum.
*This requirement may be waived when the carbon residue is more than 1.0 percent.
Sulphur—1.25 percent.
Ash—Maximum 0.10 percent.

In addition to these four, we now have and probably will see an increased market for refined kerosene for use in stoves and heaters with wick burners.

There is considerable latitude in fuel oil specifications, yet there is a tendency with some concerns to make their fuels considerably more rough and ready than even the specifications would indicate. Instead of clean distillates they work in all sorts of tank bottoms, oils from the plant separators, and others carrying moisture and sediment. From the heavier stocks a sludge may separate and settle in the customer's tank or clog his burner. Supplying an inferior grade of fuel is a poor business as many have discovered. The purchaser watches closely the results from the fuel that is put into his tank, and if he has trouble it is only natural that he should go to a brighter, cleaner grade. Profits come from repeat orders, and the practice of taking a chance on fuel oil may go far to prevent the customer from coming back. The domestic fuel business shows a good profit. It is stable and if properly fostered should show a large increase from year to year. For that reason every care should be taken to keep the fuel up to a specification which will give satisfactory results. And from a color and sediment standpoint it should be as good as it can be made. Some concerns use as much care with their domestic fuels as they do with their lubricating oils. They get the business and hold it.

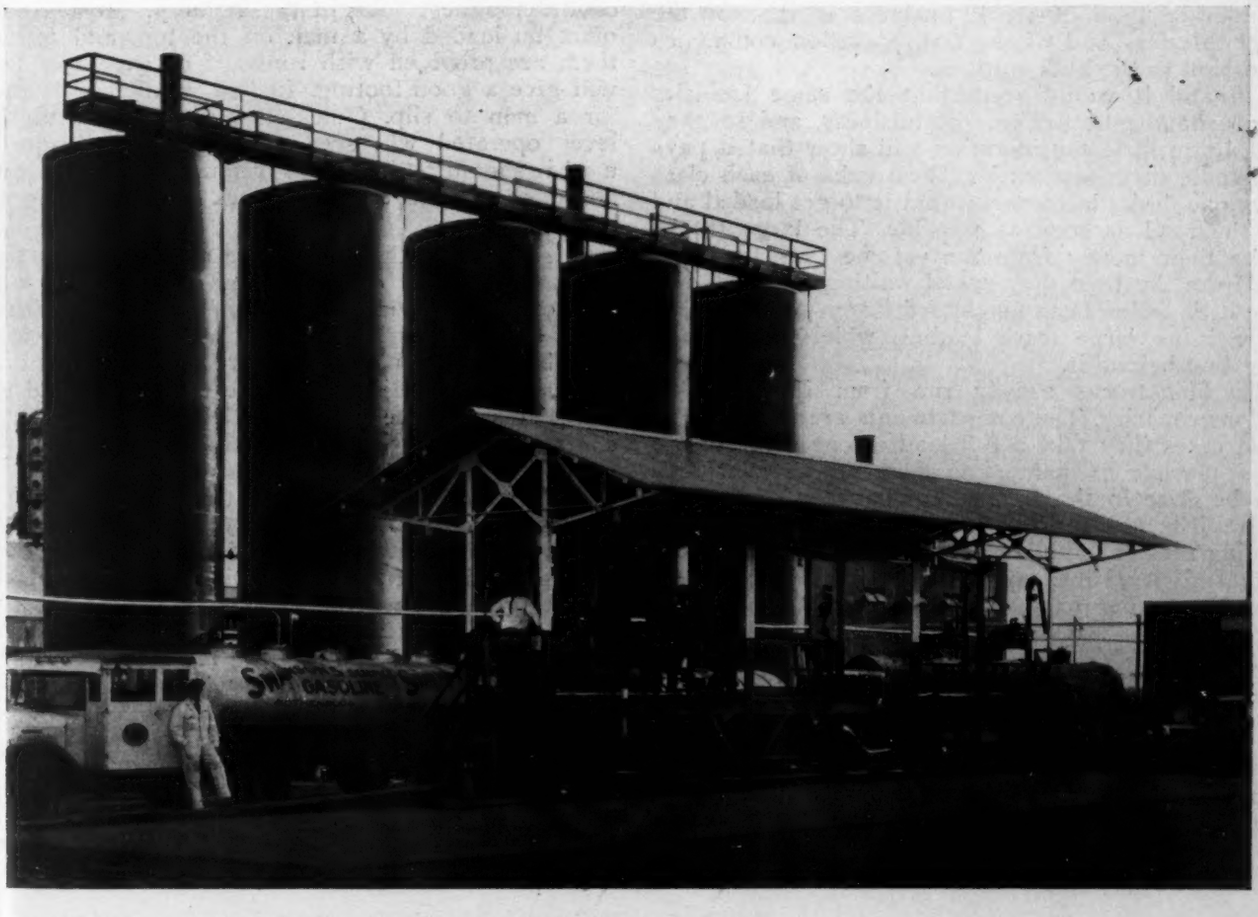
REFINERY LOADING RACK

The distribution of fuel begins at the refinery loading rack. From here it is sent out by tank car or truck. In most refineries facilities for tank car loadings are usually ample, as bulk handling by large trucks has reduced car shipments somewhat. In any event, any increase in car shipments can be cared for by extensions of existing tank car loading racks and without any change in the methods now in use. It is the movement by truck that calls for the most study and attention.

Fuel stored for the loading racks should be in fairly large tanks. It is well to have two for each grade. This fuel must be bright and free from moisture. The usual practice is to heat the oil and allow it to settle bright. This takes time and the storage should be large enough that there is always a tank ready for shipment.

One cause of delay and trouble to the men handling refinery fuel oil deliveries comes from wet oil. As the stocks come from the stills they usually carry some moisture, and when it is cold the sweating of the storage tanks will often cloud oil which would be bright under more moderate weather conditions. The usual scheme for drying a tank of oil is to hold it at a fairly high temperature, say 130° F. or higher, until it is dry and bright. Under such conditions there will be a considerable evaporation of water. This condenses on the cold top of the tank, pulls together in drops and falls back into the oil. A considerable portion of it does settle out, but in its passage down through the oil some of the dropping water is re-evaporated and the whole process is repeated. Such action slows down the drying of the oil and also consumes an excess amount of heating steam. If the tanks in which this drying is done are provided with large vents—one to three feet in diameter is not too large—most of this evaporated vapor will pass off without going back into the oil.

Sometimes there are complaints about wet oil which was bright when it was loaded into the trucks or tank cars. One cause of such trouble may be the fact that the oil was loaded at too high a tempera-



ture—120° F. to 130° F. is high enough. Above this temperature, especially if the oil is 150° F. or higher, sweating is likely to occur.

Another item which takes on added importance in the handling of the increased fuel oil output is that of forecasting demands and having fuels of the proper grades on hand as they are needed. This is especially true if the refinery is so located that barge transportation is used. Here large demands are likely to come with little or no notice. In a refinery shipping considerable volumes of varied fuels it is a good one-man job to follow up this matter. To have the oil ready, mixtures must be made and tankage provided. The oil must be dry and arrangements must be made to bring it to the proper tanks as it is needed. As a rule, only a limited number of tanks can be given over to fuel oil, and at busy times it is necessary to use considerable foresight in planning pumpings in and out of them. The regular lines of fuels will of course have their own tanks, but some extra tanks must be held for special mixes, extra large shipments, etc.

This forecast work must also cover the production of stocks from the stills and supplementing such stocks if necessary from stock in storage or by purchase so that the grades needed will be on hand for shipping.

In planning the truck loading rack the first consideration should be the character of the business. The trucking business will be of two kinds. Part of it may be small trucks handling local deliveries, carrying from 200 to 1000 gallons and having small compartments. These usually pick up their loads and deliver them direct to the house tanks of their customers. Many dealers have no storage tanks at all, but carry their entire stock direct from the tanks of the refinery or bulk station. Others have small tanks and carry sufficient storage to care for rush orders. The other type of truck business is that of the larger dealers and of the transportation companies who haul to the bulk stations.

Offhand it would seem that the same facilities would handle both kinds of business, and so they will, but a little consideration will show that it pays to handle them separately. The trucks of each class have one desire in common, that is to get loaded and on the road as soon as possible. The large trucks make their money from the volume they haul and not from the time they spend waiting to be loaded. The little fellows can be cleared faster provided that there is no large truck loading which holds up a long line behind it.

The bulk trucks usually run from 1500 to 5000 gallons capacity. The compartments are large and in most cases they take a full load of one grade of oil. It is possible to pump into them much faster than can be done in the smaller compartments. For this reason it is well to have two sections or sides to the loading rack. The bulk truck side should be provided with sufficient lines to make a quick loading. The side for smaller trucks should be arranged accordingly. In this way both sides can be kept moving and satisfied.

In addition to the lines for No. 1, 2, 3 and 4 fuels there should be a line for heavy bunker fuels and for other tar fuels. While these are not exactly domestic fuels, they are used in many apartment houses, institutions, etc., and the refinery may get considerable business from this source. There should also be a line for refined kerosene.

For everything except tar oils, centrifugal pumps are satisfactory. One advantage of this type of pump is that a line may be closed against it without damage resulting. A disadvantage is that considerable air is churned into the oil and this may give some trouble in loading.

Rotary pumps provided with relief valves set at 50 or 60 pounds work very well. It is possible to shut off against this type provided the relief valve is working, and they pick up less air than a centrifugal. For tar oils it is hard to beat a reciprocating steam pump.

In handling the heavier tar oils during cold weather the matter of temperature is an important consideration. The oil must be held at a temperature sufficiently high that when it reaches the customer it will flow well enough to pump easily. This will mean in most cases that the temperature of the loaded truck leaving the rack must be in the neighborhood of at least 130° F.

The lines from the tanks to the loading racks for these grades of oil must be kept as short as possible. They should be insulated and in many cases should be steam heated. One good method for doing this is to carry steam lines along the tar lines, binding them all together with insulation.

All tar lines during weather when the temperature is likely to drop must be blown clear back to the tank after each pumping. If the lines are long and it is not desired to do this, the hot oil may be kept circulating through a heater and back to the tank.

All fuel oil lines from the rack to the tank should be provided with air connections so that they may be blown clear when necessary.

In the design of loading rack itself, consideration should be given to the fact that in cold or bad weather the operation of the rack is likely to be one of the toughest jobs in the refinery. Most trucks must be loaded by a man on the top, and few of them are provided with runways or cat-walks that will give a good footing. In bad weather it is easy for a man to slip. Quick-closing valves should be lever operated wherever possible. Where rope is used it should be inspected frequently. Many a man has gone off the top of a truck due to the rope's breaking.

In some cases the roof of the rack is so low that the loader on the top of a large truck works with part of his body above the roof trusses and brace rods. By all rules he should climb off the truck as it is being moved up, but more often than not he moves along with it, hanging to the trusses and the rods. This practice can easily lead to serious accidents and it is advisable to fit the height of the roof to the height of the largest truck to be loaded.

Bulk stations as a rule are under the control of the sales department. In the refinery, however, owing to the operations necessary beyond that of simply loading the oil into the carrier, it is advisable that the operating department handle the fuel shipment as a part of its regular work. The contact with the sales department should be free from red tape, and a system of orders should be devised which will avoid delay on that end.

On the whole, the increase in demand for domestic fuels has brought in few really new problems. It must be recognized, however, that for real efficiency the various items entering into the handling of these fuels must be grouped by themselves and operated as a unit.

Convenient Calorimetric
Hydrogen Ion Kit

By HAROLD BOTTOMLEY,
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MORE and more are hydrogen ion determinations coming into use in the petroleum industry. The haphazard methods of former years are giving way to closer methods of control over solutions, additions of reagents, control of acidity and alkalinity in distillation unit streams, condensing water, etc.

Probably the most facile of pH apparatus is the electrometric, but in many cases the investment is of doubtful payout until pH control is definitely established as a permanent thing. Below is described a colorimetric pH kit which involves no new theory or originality, but directions for its construction are explicit and its cost is low.

The buffer solutions and indicators used are those given by Clark and Lubs (Scotts, Standard Methods of Chemical Analysis, 1925 p. 1430) with some modifications to simplify the preparation.

The reagents and their preparation follow:

M/5 Potassium Hydrogen Phthalate, Eastman grade, purified by two crystallizations from distilled water. Dried at 110° C. to constant weight. Use 40.83 grams per liter.

M/5 Potassium Chloride, any good reagent quality recrystallized twice from distilled water and dried at 120° C for 24 hours. M/5 solution contains 14.91 grams per liter.

M/5 Potassium Hydrogen Phosphate, recrystallize high quality reagent grade twice from distilled water and dry at 110° C for 24 hours. An M/5 solution contains 27.23 grams per liter.

M/5 Boric Acid, recrystallize reagent grade twice from distilled water and dry at 50° C to constant weight. M/5 solution contains 12.405 grams per liter.

M/5 Sodium Hydroxide. Highest quality NaOH free from carbonate should be used for this solution and a factor is preferable to exact manipulation of the molarity. This solution should be made up as needed and an M/5 solution contains 8 grams per liter.

For use the M/5 KCl and M/5 H_3BO_3 are mixed 50-50 for incorporation into the buffers. The solutions are made up below as follows. The measurements should be made with accurately calibrated burettes.

pH	Amount cc.	Reagent	Amount cc.	Reagent
4.4	50	M/5 KH phthalate	7.5	M/5 NaOH
4.6	50	M/5 KH phthalate	12.15	M/5 NaOH
4.8	50	M/5 KH phthalate	17.70	M/5 NaOH
5.0	50	M/5 KH phthalate	23.85	M/5 NaOH
5.2	50	M/5 KH phthalate	29.95	M/5 NaOH
5.4	50	M/5 KH phthalate	35.45	M/5 NaOH
5.6	50	M/5 KH phthalate	39.85	M/5 NaOH
5.8	50	M/5 KH phthalate	43.00	M/5 NaOH
6.0	50	M/5 KH phthalate	45.45	M/5 NaOH
6.2	50	M/5 KH_2 phosphate	8.60	M/5 NaOH
6.4	50	M/5 KH_2 phosphate	12.60	M/5 NaOH
6.6	50	M/5 KH_2 phosphate	17.80	M/5 NaOH
6.8	50	M/5 KH_2 phosphate	23.65	M/5 NaOH
7.0	50	M/5 KH_2 phosphate	29.63	M/5 NaOH
7.2	50	M/5 KH_2 phosphate	35.00	M/5 NaOH
7.4	50	M/5 KH_2 phosphate	39.50	M/5 NaOH
7.6	50	M/5 KH_2 phosphate	42.80	M/5 NaOH
7.8	50	M/5 KH_2 phosphate	45.20	M/5 NaOH
8.0	50	M/5 KH_2 phosphate	46.80	M/5 NaOH
8.2	50	M/5 H_3BO_3, KCl	5.90	M/5 NaOH
8.4	50	M/5 H_3BO_3, KCl	8.50	M/5 NaOH
8.6	50	M/5 H_3BO_3, KCl	12.00	M/5 NaOH
8.8	50	M/5 H_3BO_3, KCl	16.30	M/5 NaOH
9.0	50	M/5 H_3BO_3, KCl	21.30	M/5 NaOH
9.2	50	M/5 H_3BO_3, KCl	26.70	M/5 NaOH
9.4	50	M/5 H_3BO_3, KCl	32.00	M/5 NaOH
9.6	50	M/5 H_3BO_3, KCl	36.85	M/5 NaOH
9.8	50	M/5 H_3BO_3, KCl	40.80	M/5 NaOH
10.0	50	M/5 H_3BO_3, KCl	43.90	M/5 NaOH

Note:—Dilute each to 200 cc. with freshly boiled distilled water.

These stock buffer solutions are apparently fairly permanent. Those in use at our laboratory show no appreciable deterioration after 3 years storage in the dark. Twenty-five cc. of each of these buffers were measured into individual one ounce soft glass homeopathic vials and 12 drops of the particular indicator (to be described below), added to each of the tubes. One drop of toluol was added to each, to prevent mold, the tubes corked and the corked ends dipped into melted paraffin wax.

The indicators used with this kit are:

Methyl red, pH range 4.4 to 6.0; Brom thymol blue, pH range 6.2 to 7.4; Cresol red, pH range 7.6 to 8.8; Thymol blue, pH range 9.0 to 10.0; and were made up as follows: *Methyl red,* 0.1 gram of methyl red powder is macerated in a mortar with 7.4 cc. of N/20 sodium hydroxide and then made up to 500 cc. with distilled water which gives a .02 percent solution. *Brom Thymol Blue,* 0.1 gram of this material whose correct name is dibromothymolsulfonphthalein is ground with 3.2 cc. of N/20 NaOH and then diluted to 250 cc. which is a .04 percent solution. *Cresol Red* (ortho-cresol sulfonphthalein) is ground with 5.3 cc. of N/20 NaOH and diluted to 500 cc. *Thymol Blue* (thymolsulfonphthalein) is ground with 4.3 cc. of N/20 NaOH and diluted to 250 cc.

It is preferable that these indicators be kept in subdued light. The prepared standards with added indicators begin to deteriorate in about one month after preparation, the methyl red series being by far the worst offender. However if a 200-cc. stock of buffer is kept on hand it is but the work of a few moments to renew the entire working range.

To use, the sample whose pH is to be determined is placed in a vial like those containing the standards and 12 drops of the proper indicator added. Then all that is necessary is to compare the unknown with the correct standard tube. Interpolation to 0.1 pH is an easy matter. If the unknown contains suspended material or is turbid, a vial filled with the unknown and held in line with the standard will facilitate matching the colors.

This pH kit has been used for several years (with renewals now and then) in the control of condenser water alkalinities and in the control of ammonia additions to corrosive petroleum distillate streams. The cost of the outfit will not exceed $10.00.

Metering Gas *and* Oil

The Significance of Reynolds' Number in the Measurement of Fluid Flow

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UNTIL recent years, practically no data was available on the measurement of viscous fluids with orifices, nozzles, or other forms of head meters. It is true, of course, that some research had been conducted along this line, but the information available was meager and indefinite. In most cases investigations in the field of viscous fluids have been conducted with small size apparatus. The extrapolation of this data, in an attempt to make it applicable to lines of commercial size, introduced questionable factors to such an extent that the result was little better than an approximation. With the rapid growth of the petroleum industry and with the introduction of modern methods a need for accurate data on fluid meters has developed. This need must be satisfied.

In an effort to circumvent the difficulties caused by the lack of accurate data, many substitutes for the simple head meter have been accepted. Some of these substitutes have definite merits while others are cumbersome, inaccurate, and altogether make-shift. For the benefit of all concerned, a more popular knowledge of viscosity and its effect on the flow of fluids is to be desired.

In the year 1883, Osborne Reynolds proposed the "Number," which today bears his name, as the logical index to the conditions of flow prevailing in a pipe. This criterion of flow has been proven theoretically and experimentally to be the correct basis upon which to correlate fluid flow data. For example, orifice meter coefficients determined with various dissimilar fluids over a wide range of viscosity, yield consistent data which, when plotted, forms a single smooth curve. A typical curve representing this variation is shown in Figure 2.

The term "Reynolds number" quite generally has been clothed in an almost medieval mysticism. This awe with which the term has been regarded is quite unnecessary and in fact quite undesirable. For it is not until the significance of the term is more generally understood, that we may expect more general assimilation of the fluid flow data that is today available. The American Gas Association in a recent publication has indicated that even the orifice meter flow constants for gas—which had previously been taken as constant—are a function of Reynolds' number.

The "number" which Reynolds proposed is essentially a very simple expression. Based upon his observations, he stated that the properties of flow should be a direct function of a linear dimension, the fluid velocity, and the density and should vary inversely with the fluid viscosity. The most logical linear dimension, in the case of fluid measurement, is the diameter of the opening in the head meter; correspondingly, the fluid velocity considered, should be that prevailing at that same section. It is interesting

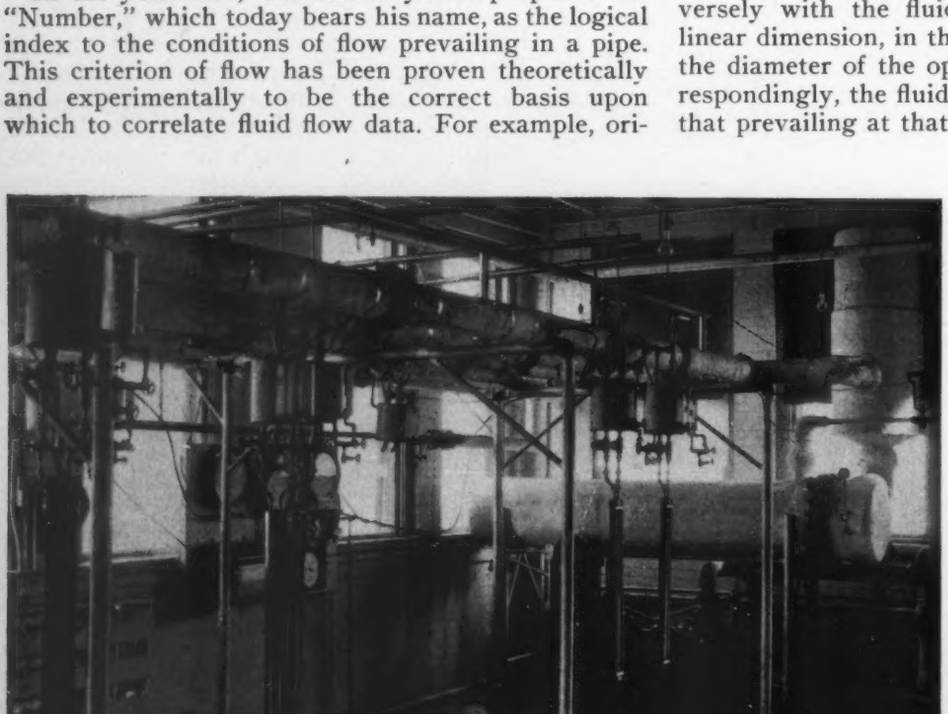


FIGURE 1

View of test apparatus used in fluid meter testing at the University of Oklahoma. Tests are conducted on commercial sizes of lines at flow rates as high as 750 barrels per hour.

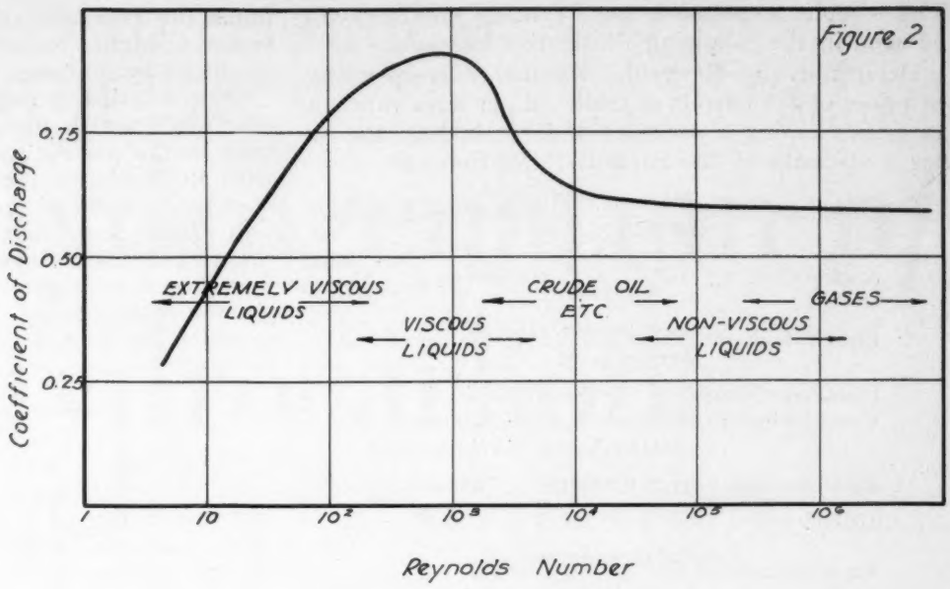


FIGURE 2

to observe that if the dimensions of all the component factors in the Reynolds' number be considered; diameter—feet, velocity—feet per second, density—pounds per cubic foot, and absolute viscosity—pounds per foot per second; all the dimensions will cancel—indicating that Reynolds' number is non-dimensional. Since Reynolds' number has no dimensions, any consistent system of units — English, metric, or any other—can be used with results that are numerically identical. This happy fact indicates that Reynolds' number, in addition to being sound theoretically, is a logical basis for the correlation of our data with the data obtained abroad.

The one factor in the criterion proposed by Osborne Reynolds which, from all appearances, is the greatest stumbling block, is the absolute viscosity. The following discussion will be made in an effort to clarify this term. Viscosity is a measure of the internal friction of a fluid. A fluid is said to be viscous, or possessed of high viscosity, when it tends to resist motion produced by an outside force. A glass containing molasses, when tilted from an upright position, will assume a new fluid level very slowly. The fluid level of water, however, adjusts itself very rapidly to changes caused by a change in position of the containing vessel. The two liquids represent limits of an extreme range in fluid viscosity.

A discussion of the mechanics of fluid viscosity may result in a more fundamental conception of the significance of the term. Since the absolute viscosity is a measure of the internal friction of the fluid it is logical to analyze this frictional property in the same manner in which mechanical friction would be considered. Let it be assumed that a flat plate, parallel to a rigid plane surface, is moving at a constant velocity. The flat plate and the plane surface are separated by a number of thin layers of the fluid. Of these fluid layers, the one adjacent to the flat plate adheres to the plate and consequently moves with the same velocity as the plate, while the layer adjacent to the rigid plane surface is stationary. Each of the other fluid layers is moving with a speed different from that of its neighbor, with consequent relative motion between all the layers. Frictional resistance is encountered between each of these fluid layers, consequently, the maximum fluid velocity is always attained at a point in the fluid stream farthest from the retarding influence of the channel walls.

The common index to fluid viscosity is the indication obtained from a Saybolt Universal Viscosimeter. In Figure 3 a sketch of the essential parts of this instrument is shown. The Saybolt viscosity is the time in seconds required for 60 cubic centimeters of the fluid to flow through a capillary tube. For very viscous fluids, the tip containing the capillary tube may be replaced with a Furol tip containing a larger tube which permits the fluid to flow 10 times as fast. With this larger capillary tube the Saybolt "Furol" time viscosity is obtained which is one tenth of the Saybolt "Universal" time viscosity. It is obvious that with this instrument the force effective for producing flow through the capillary tube is a direct function of the fluid density. If two fluids having the same internal fluid friction or viscosity were allowed to flow through the instrument, the fluid having the greatest density would flow the fastest. This time viscosity is consequently not a measure of the absolute viscosity, but rather a measure of the absolute viscosity divided by the density of the fluid. This ratio of absolute viscosity to density has been assigned the term—kinematic viscosity. This kinematic viscosity is related to the Saybolt time viscosity according to the following equation:

$$\text{Kinematic viscosity} = 0.00000237t - \frac{0.00194}{t}$$

where "t" is the time viscosity in Saybolt Universal seconds.

Since the kinematic viscosity and not absolute vissocity is indicated by the Saybolt instrument, the calculation of the Reynolds' number is simplified.

As has been previously stated:

$$\text{Reynolds' number} = \frac{\text{Diameter} \times \text{Velocity} \times \text{Density}}{\text{Absolute Viscosity}}$$

and, dividing by the Density

$$\text{Reynolds number} = \frac{\text{Diameter} \times \text{Velocity}}{\frac{\text{Absolute Viscosity}}{\text{Density}}}$$

$$\text{but, since } \frac{\text{Absolute Viscosity}}{\text{Density}} = \text{Kinematic Viscosity}$$

$$\text{Reynolds' number} = \frac{\text{Diameter} \times \text{Velocity}}{\text{Kinematic Viscosity}}$$

This simpler expression for Reynolds' number will be used in the following illustrative example.

Determine the Reynolds' Number corresponding to a flow of 275 barrels of crude oil per hour through an orifice having a diameter of three inches; the oil has a viscosity of 300 Saybolt Furol Seconds.

$$275 \text{ bbl. per hr.} = \frac{275 \times 42 \times 231}{60 \times 60 \times 1728} = 0.429 \text{ cu. ft. per sec.}$$

$$\text{Area of Opening} = \frac{3.1415 \times 3^2}{4 \times 144} = 0.0491 \text{ sq. ft.}$$

$$\text{Fluid Velocity} = \frac{\text{cu. ft. per sec.}}{\text{Area in sq. ft.}} = 8.74 \text{ ft. per second.}$$

Diameter of Opening = 3 inches = 0.25 feet.
Viscosity index = 300 Saybolt Furol Seconds
= 3000 Saybolt Universal Seconds

$$\text{Kinematic Viscosity} = 0.00000237 \times 3000 - \frac{0.00194}{3000} = 0.007109$$

$$\text{Reynolds' number} = \frac{0.25 \times 8.74}{0.007109} = 307$$

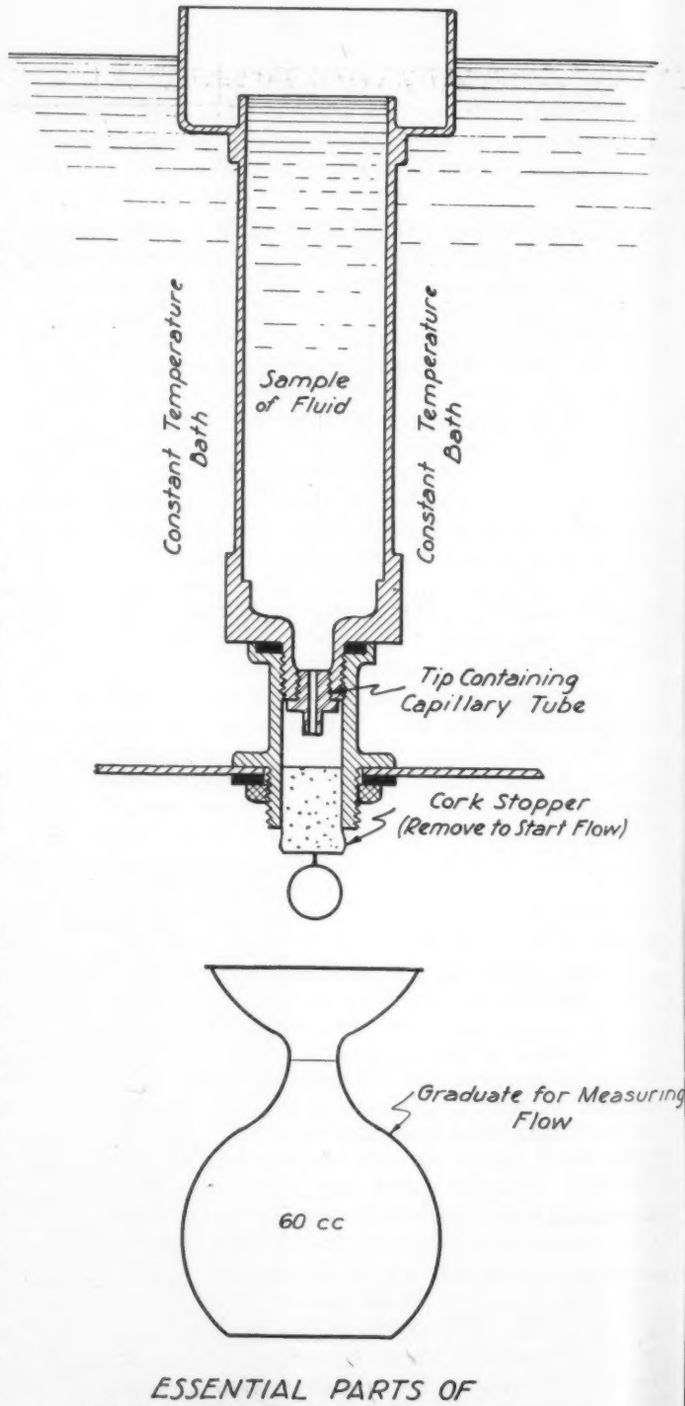
In a manner essentially the same as that indicated in the above example, Reynolds' number determinations may be made directly from the flow observations by setting up an equation where a single constant contains all the conversions lumped together. For example:

$$\text{Reynolds' number} = 0.02381 \times \frac{\text{Flow in Barrels per hour}}{\text{Diameter in in.} \times \text{Kinematic Viscosity}}$$

It is common knowledge that the viscosity of liquids decrease with increasing temperatures. Consequently, it is quite important that the fluid viscosity at the flowing temperature be known. A logarithmic plotting of kinematic viscosity against temperature will result in a substantially straight line. An extension of the straight lines representing the viscosity temperature variations will, for a variety of different fluids, intersect in practically a common point; indicating substantially a constant viscosity at about 800° F. Use of this fact is often made in preparing tables of factors for correcting the viscosity taken at some base temperature to the viscosity at the flowing temperature.

For the same reason that a knowledge of the viscosity of a viscous fluid is necessary in the calculation of Reynolds' number, the viscosity of a non-viscous liquid or that of a gas must be known. The absolute viscosity of water at 68°F. has been determined as 0.000672 pounds per foot per second with the absolute viscosity of an average natural gas listed as about 0.0000069 pounds per foot per second. Gases differ from liquids with respect to their change in viscosity with temperature variation; increasing instead of decreasing with rising temperatures. It is obvious that the viscosity of non-viscous liquids and gases must be determined with apparatus other than the Saybolt instrument. Although there is a definite change in viscosity with temperature and this change would have to be known to accurately determine the Reynolds' number, this variation is ordinarily disregarded with non-viscous liquids and gases. The neglect of this variation is warranted since the degree of variation is less and since with these non-viscous fluids the characteristics of flow are lodged in the region of higher Reynolds' numbers where the effect produced by a change in viscosity is quite small.

In conclusion it might be stated that the perfect confidence which physicists and research engineers have in the perfect variation of flow characteristics with Reynolds' number is evidenced in the manner of determination of the new American Gas Association orifice flow constants for gas. The orifice discharge coefficients upon which these flow constants were based were determined with flow tests on water, the results being then extended into the region, in which the flow characteristics of a gas are located.



ESSENTIAL PARTS OF THE SAYBOLT VISCOSIMETER

FIGURE 3

THEORETICAL AND TECHNICAL FOUNDATIONS OF THE

Hydrogenation *of* Hydrocarbons

RAFAEL FUSSTEIG,
Jaroslaw, Poland

THE demand for light liquid hydrocarbons has been so great during the past few years that oil technologists have been searching intensively all possible methods to increase production. One result of these studies has been the development of what is known generically as the hydrogenation process. This sort of the hydrogenation differs entirely from the simple hydrogenation process. By simple hydrogenation is meant solely the addition of hydrogen to the molecule without any derangements of basic construction. Destructive hydrogenation is a combination of simple hydrogenation and pyrolysis, the simple hydrogenation taking place after the rupture of the molecule. In other words destructive hydrogenation is a combination of the cracking process and simple hydrogenation.

The essential characteristic of the cracking process lies in the fact that always there is formed along with the light hydrocarbons, products being enlarged in statu nascendi with hydrogen, split from the second part of the molecule, and as the crude oil contains about 14 percent of the disposable hydrogen, this second part of the split molecule is transformed into polymerized heavier hydrocarbons, such as tar and coke. In destructive hydrogenation these polymerization processes may be prevented so that only light products are made. In other words the addition of hydrogen in the moment of the splitting of the molecules prevents the polymerization and condensation of the unsaturated hydrocarbons.

For this purpose high temperatures and pressures must be employed, the obtained reactions being dependent upon these factors. These reactions can be easily determined by means of the mathematical expression of Nernst:

$$\lg K = \frac{Q}{4.57.T} - n.1.75.\lg T - n.C$$

Q=the heat of vaporization of the given reactions.

n=the algebraic total of molecules taking part in the reaction, the disappearing molecules being denoted by the plus sign and the appearing molecules by the minus sign.

n.C=the algebraic total of products of the chemical constants by number of molecules.

These calculations show that the values of lg.K for olefins are positive even at 477°C.; that is to say that the addition of the hydrogen into the olefins can be easily carried out. As the values of lg.K at 200°C. are very great this addition can be carried out without great pressures. However, the addition of cyclic and aromatic hydrocarbons shows another character. The values of lg.K for these reactions are positive only at the temperature of 200°C. At temperatures above 300°C., the cyclic and aromatic compounds show a negative value which brings about the reversible process of dehydration. High pressures must therefore be used to obtain the equilibrium constant of these reactions. According to this phenomena it is very easy to hydrogenate only the unsaturated hydrocarbons of the petroleum oils, the aromatic hydrocarbons being unattached because of using a lower pressure.

In order to prove the correctness of these theoretical considerations a fraction which contained a great number of olefins has been hydrogenated. The physical characteristics of this fraction are as follows

Specific gravity/15°C	0.803.
Boiling point	154°C.
Endpoint	293°C.
Content of olefins	63%
Content of aromatic compounds	7%

In the first experiments this fraction was submitted to the hydrogenation process without use of catalysts. Table 2 shows the results.

It can be seen from Table 2 that the process proceeds very slowly, having in consequence only the transformation of 50 percent of olefins into saturated hydrocarbons. The same fraction was then submitted to the hydrogenation process by using different catalysts. The results are shown in Table 3.

Considering the results in Table 3, it can be seen

TABLE 1

Reactions:	Heat of Vaporization	LOG K		
		At 200°C.	At 300° C.	At 477° C.
$C_6H_{12}+H_2=C_6H_4$ (Hexane)	32,000 Cal.	+ 8.5	+ 6.1	+ 2.6
$C_{12}H_{24}+H_2=C_{12}H_{26}$ (Dodecane)	36,000 Cal.	+10.6	+ 7.5	+ 4.1
$C_{16}H_{32}+H_2=C_{16}H_{34}$ (Hexadecane)	37,000 Cal.	+11.2	+ 8.0	+ 4.4
$C_6H_6+3H_2=C_6H_{12}$ (Cyclohexane)	54,000 Cal.	+ 5.2	+ 0.3	— 4.0
$C_{10}H_8+5H_2=C_{10}H_{18}$ (Decaline)	74,000 Cal.	+ 2.9	— 3.9	—11.4
$C_{10}H_8+2H_2=C_{10}H_{12}$ (Tetraline)	30,000 Cal.	+ 1.4	— 1.3	— 4.4
$C_{10}H_{12}+3H_2=C_{10}H_{18}$ (Decaline)	44,000 Cal.	+ 1.6	— 2.5	— 7.1

TABLE 2

Experiment:	1	2	3	4	5
Initial Pressure	98 Atm.	101 Atm.	99 Atm.	101 Atm.	100 Atm.
Maximum Pressure	272 Atm.	278 Atm.	275 Atm.	275 Atm.	276 Atm.
Pressure after reaction	45 Atm.	48 Atm.	42 Atm.	45 Atm.	38 Atm.
Reaction Temperature	245°C.	250°C.	252°C.	250°C.	262°C.
Time of Hydrogenation	90 Min.	100 Min.	95 Min.	98 Min.	95 Min.
Characteristics after Hydrogenation:					
Specific Gravity	0.775/15	0.769/15	0.771/15	0.765/15	0.769/15
Aromatic Compounds	7%	6.8%	7%	7.2%	7.1%
Olefins	35%	37.0%	40.0%	40.0%	42.0%

TABLE 3

Experiments:	6	7	8	9	10
Catalysts	Mn+Co+Cu	Ni+Co+Cu+Mo	Fe_2O_3+Ni	Ni_2O_3+Mno_2	Mns_3+Co_3O_3+MnO_3
Quantity	4.2 %	3.9%	4.5%	5.0%	3.8%
Pressure after Reaction	47 Atm.	55 Atm.	61 Atm.	58 Atm.	49 Atm.
Maximum Pressure	297 Atm.	289 Atm.	275 Atm.	280 Atm.	292 Atm.
Time of Hydration	62 Min.	58 Min.	61 Min.	58 Min.	49 Min.
After the Process:					
Specific Gravity	0.755	0.742	0.748	0.753	0.742
Aromatics	7.2%	7.2%	6.5%	6.8%	6.5%

TABLE 4

The experiments with the same catalysts mixed with fuller's earth

Experiments:	11	12	13	14	15
Maximum Pressure	281 Atm.	280 Atm.	286 Atm.	285 Atm.	283 Atm.
Initial Pressure	91 Atm.	94 Atm.	96 Atm.	96 Atm.	95 Atm.
Pressure after Reaction	50 Atm.	55 Atm.	52 Atm.	54 Atm.	53 Atm.
Time of the Process	45 Min.	42 Min.	44 Min.	45 Min.	43 Min.
After the Reaction:					
Specific Gravity/15	0.728	0.732	0.730	0.731	0.730
Aromatics	7.2%	7.2%	7.5%	6.9%	7.1%
Olefins	.....	.....	.....	.....	.....

TABLE 5

Experiments:	16	17	18	19	20
Catalyst	Ni+Co	Ni+Ni_2O_3	MnS_3	Mo+Ni	MnS_3+Mo
Mixed with	.....	.....	.....	Fullers Earth	Fullers Earth
Quantity of Catalyst	6%	5%	5%	4%	3.5%
Initial Pressure in Atm.	105	110	109	98	95
Maximum Pressure in Atm.	252	260	250	232	220
Pressure after Reaction	75	72	48	52	44
Time of Reaction, in Min.	140	145	120	78	65
Temperature of Reaction	455°C.	428°C.	432°C.	435°C.	438°C.
Yield of Raw Gasoline	65%	72%	88%	91%	98%
Specific Gravity of Gasoline	0.752/15	0.745/15	0.720/15	0.715/15	0.706/15
Color—Colorless					
Yield:					
Gasoline to 200°C.	30.5%	36%	46.2%	54%	61.2%
Residuum	62.7%	60%	48.0%	31%	36.0%
Coke	Traces	Traces	.....	Traces	.....
The Rect. Gasoline Contains:					
Olefins	2.5%	1.5%	.....	.....	.....
Aromatics	4.2%	4.5%	4.2%	6%	5.1%

that the presence of catalysts accelerated the velocity of hydrogenation. After a time of 70 minutes only 14 percent of the olefins remained unattacked. Of course the aromatic hydrocarbons remained unattacked as well. The activity of the above mentioned catalysts can be raised by mixing them with fuller's earth. In this case an enlargement of the surface of efficiency takes place.

The results in Table 4 show that the enlargement of the surface of efficiency brought about the entire hydrogenation of olefins, the time of the operation being lowered to 45 minutes. As shown in the same table the aromatic hydrocarbons remained unattacked on account of insufficient velocity of reaction.

The saturated hydrocarbons show a quite different conduct as they are first split in little molecules which are then completed with hydrogen. The splitting complicates with the increase of molecular weight, because their content of hydrogen decreases. Therefore temperature and pressure must be increased to obtain the hydrogenation point. Without the increase of these two factors the velocity of the reaction is too small, and the process will pass in the direction of formation of gaseous hydrocarbons on the one side, and of liquid dehydrated, unsaturated hydrocarbons which easily polymerize into tar and coke, on the other side. Therefore it is necessary to increase the reaction of hydrogenation in that manner that the split dehydrated hydrocarbons can be easily completed with hydrogen in the moment of their statu nascendi. The reaction of hydrogenation will be increased by using corresponding catalysts.

The catalysts always must be employed, because even the highest pressures are unable to obtain the necessary reactions. The use of a catalyst at a temperature of 450°C., and pressure of 200 Atm., brings about a result that cracking and hydrogenation are increased to a high degree. In order to prove the correctness of these theoretical considerations, an oil has been extracted from the unsaturated hydrocarbons by means of the Edeleanu process. Table 5 shows the results.

It can be seen from Table 5 that the sort of catalyst influences to a high degree the process of hydrogenation. A mixture of Ni+Co secured a gasoline yield of 65 percent, whereas the using of a mixture of MnS + Mo resulted in the gasoline yield of 98 percent. In the experiments 16, 17 and 19, traces of coke have been observed, being in consequence of the inuence of nickel. The catalyst effect on saturated hydrocarbons can be expressed as follows:

1. A reduction of the optimum temperature for a favorable yield of gasoline will be obtained by means of the acceleration of the molecule rupture.

2. Highly saturated hydrocarbons will be obtained by means of the acceleration of the hydrogen addition. This because the hydrogen addition runs parallel with the velocity of the rupture.

As seen in Table 5 the aromatic hydrocarbons remained unaltered to about 70 percent, the rest being transformed into benzol, cyclohexane, etc.

Let us observe the hydrogenation process of the mixed groups of hydrocarbons. Kerosene, gas oil, lubricating oils could be considered as the representatives of such mixtures. The hydrogenation of kerosene and gas oil can be carried out easily, because the split molecules are completed with hydrogen. In this case it is sufficient to carry out the hydrogenation in the so called one-phase system. Table 6 shows the hydrogenation of kerosene and gas oil.

The results in Table 6 show that the yield of gasoline decreases with the increase of the molecular weight of hydrocarbons. In other words it can be said that the higher the molecular weight, the more difficult it is to complete the splitting molecules with hydrogen. According to the conditions of this hydrogenation treatment and the nature of the catalysts employed, the chemical reactions that occur alter their direction, and therefore only polymerization and condensation of the splitting molecules take place. Therefore the hydrogenation process of higher molecular weight hydrocarbons apparently should be carried out in two phases: in the first liquid-phase treatment, the higher molecular weight hydrocarbons will be split and hydrogenated into middle molecular compounds, these being then split and hydrogenated in the second vapor-phase. The catalyst is indeed able to transform the higher molecular weight hydrocarbons into gasoline at the beginning of the process, but it can be seen that as soon as the partial pressure and the throughput increase the activity of the catalyst will quickly decrease. These results are presented in Table 7.

If we consider the results of Table 7, it is quite evident that the hydrogenation of the higher molecularg weight hydrocarbons cannot be carried out directly. These difficulties arise for two reasons: 1. The higher molecular compounds of the charging stock are adsorbed by the surface of the catalyst in the beginning of the process, contributing, in consequence, to the isolation of the rest of hydrocarbons. 2. The higher molecular compounds are dehydrated and polymerized at a higher partial pressure. Therefore these compounds will be transformed into hydrocarbons which can not be split, being finally held back on the surface of the catalyst. These reactions cause the decrease in activity of catalysts.

To obviate these difficulties the process can be

TABLE 6

Experiments:	21	22	23
Charging Stock	Kerosene	Light Gas Oil	Heavy Gas Oil
Specific Gravity/15°C	0.823	0.832	0.861
Olefins	5.8%	8%	7.2%
Aromatics	18.3%	22%	38.1%
Catalyst	Ni_2O_3+MnO	MnO+MoS_3	Ni+Mn+MoS_3
Percent	4.5%	5%	5%
Initial Pressure in Atm.	95	102	105
Operating Pressure in Atm.	225	235	258
Pressure after Reaction Atm.	58	63	62
Time of Reaction in Min.	65	72	70
Temperature of Reaction	450°C.	472°C.	485°C.
Yield of the Raw Gasoline	88%	90.5%	88%
Specific Gravity/15°C	0.742	0.795	0.806
Color	Colorless	Light Yellow	Light Yellow
Olefins	2.2%	4.2%	2.8%
Aromatics	18.2%	14.0%	16.0%
Coke after Hydrogenation	Traces	.....	Traces

TABLE 7

Experiments:	24	25	26	27	28
Viscosity/E°/50°C	3-4/50	5-6/50	8-10/50	4-5/100	Asphalt
Specific Gravity/15°C	0.895	0.903	0.908	0.928	1.08
Olefins	10.5%	12%	11%	18.5%	16.3%
Aromatics	6.2%	9.5%	8%	25%	13%
Tar acc. M. A. V.	18.2%	25.4%	29%	35%	78%
Catalyst—a 4% Mixture of MoS_3+Fe_2O_3+Ni_2O_3+Mn in silicate					
Initial Pressure in Atm.	115	115	98	102	101
Maximum Pressure in Atm.	258	265	260	260	272
Pressure after Reaction Atm.	75	72	68	65	73
Time of Process in Min.	85	85	80	82	90
Temperature of Reaction°C	452	450	480	475	455
Yield of Gasoline	35%	28%	28%	26%	15%
Yield of Residuum	54%	60%	59%	61%	70%
Characteristics of Gasoline:					
Specific Gravity/15	0.752	0.753	0.763	0.758	0.749
Olefins	4.8%	6.3%	3.2%	8.4%	9.5%
Aromatics	4.2%	18.4%	5.5%	12.0%	10.2%
Characteristics of Residuum:					
Specific Gravity/15	0.945	0.958	0.960	0.965	0.999
Coke	Traces	Traces	.....	0.08%	3.25%
Olefins	12.5%	16.3%	9.5%	16.0%	18.3%
Aromatics	3.2%	4.8%	4.2%	23%	9.4%

divided into two stages, liquid phase and vapor phase. Separation of the process into stages serves to eliminate both of the above difficulties.

A corresponding catalyst must be employed for each phase. The catalyst used for the liquid-phase hydrogenation must maintain a satisfactory hydrogen concentration, because a great velocity of hydrogenation is necessary at the temperature of 300°C. to prevent the dehydration and polymerization of the split higher molecular weight hydrocarbons. The catalyst depends somewhat upon the nature of the raw materials and usually is added in admixture with the charging stock.

The process of the vapor-phase hydrogenation depend to a high degree upon a variety of factors. For example, the temperature and the pressure of hydrogen influences the degree of hydrogenation this being increased by increasing the hydrogen pressure, and decreased by raising of temperature. The catalyst is able to transform all split molecules into gasoline of high quality. It is suspended inside the converters and selection is based upon the nature of the final products desired. By careful control of temperature, pressure, catalyst, and time of reaction, it is possible to produce products of high quality.

A great inconvenience of the hydrogenation process is the rupture of oxygen, sulfur and nitrogen from the molecule and transformation into water, hydrogen sulfide and ammonia. These last two compounds are adsorbed on the surface of the catalyst causing poisoning of the catalyst. But the researches of the chemist have resulted in the development of a iarge number of catalysts. It is known, that the development of nonpoisoning catalysts has resulted in the extensive use of metallic sulfides, especially those of molybdenum, tungsten and cobalt. The writer recommends the use of molybdenum sulfide mixed with the compounds of the oxides of iron, nickel and cobalt.

According to the conditions and the nature of the catalysts employed the chemical reactions that occur alter their direction and extent. The use of the mixture mentioned above resulted in a favorable rupture of the impurities without poisoning of the catalyst. The alien elements oxygen, sulfur and nitrogen have been preferentially attacked by the hydrogen so vigorously that they leave the reaction zone as the corresponding gaseous hydrides.

The principles and the practical application of this process have been the subject of research and development of a new industry. Experience gained on the operation of the commercial plants has indicated that the same unit may be used for either low-temperature or high-temperature hydrogenation by adjusting the reaction chamber and by using different catalysts. But only hydrogen has been employed in the hydrogenation process. Nobody has considered methane, a gas to be found in great quantities, as a hydrogenation material. This gas is very rich in hydrogen, and considering it from the theoretical standpoint, it is possible under certain conditions to polymerize it into gasoline hydrocarbons liberating at the same time a great deal of hydrogen:

$$2CH_4 \rightarrow C_2H_6 + H_2$$
$$C_2H_6 + CH_4 \rightarrow C_3H_8 + H_2$$
$$2C_2H_6 \rightarrow C_4H_{10} + H_2$$
$$2C_4H_{10} \rightarrow C_8H_{18} + H_2$$
$$2C_8H_{18} \rightarrow C_{16}H_{34} + H_2$$

Investigations have established that the hydrogenation between the split molecules of methane and the split higher molecular hydrocarbons can be carried out easily if the proper catalyst, pressure and temperature are used. In this case not only the polymerization of the split parcels of methane and the hydrogenation of the split hydrocarbons will be produced; the chemical reaction between the split

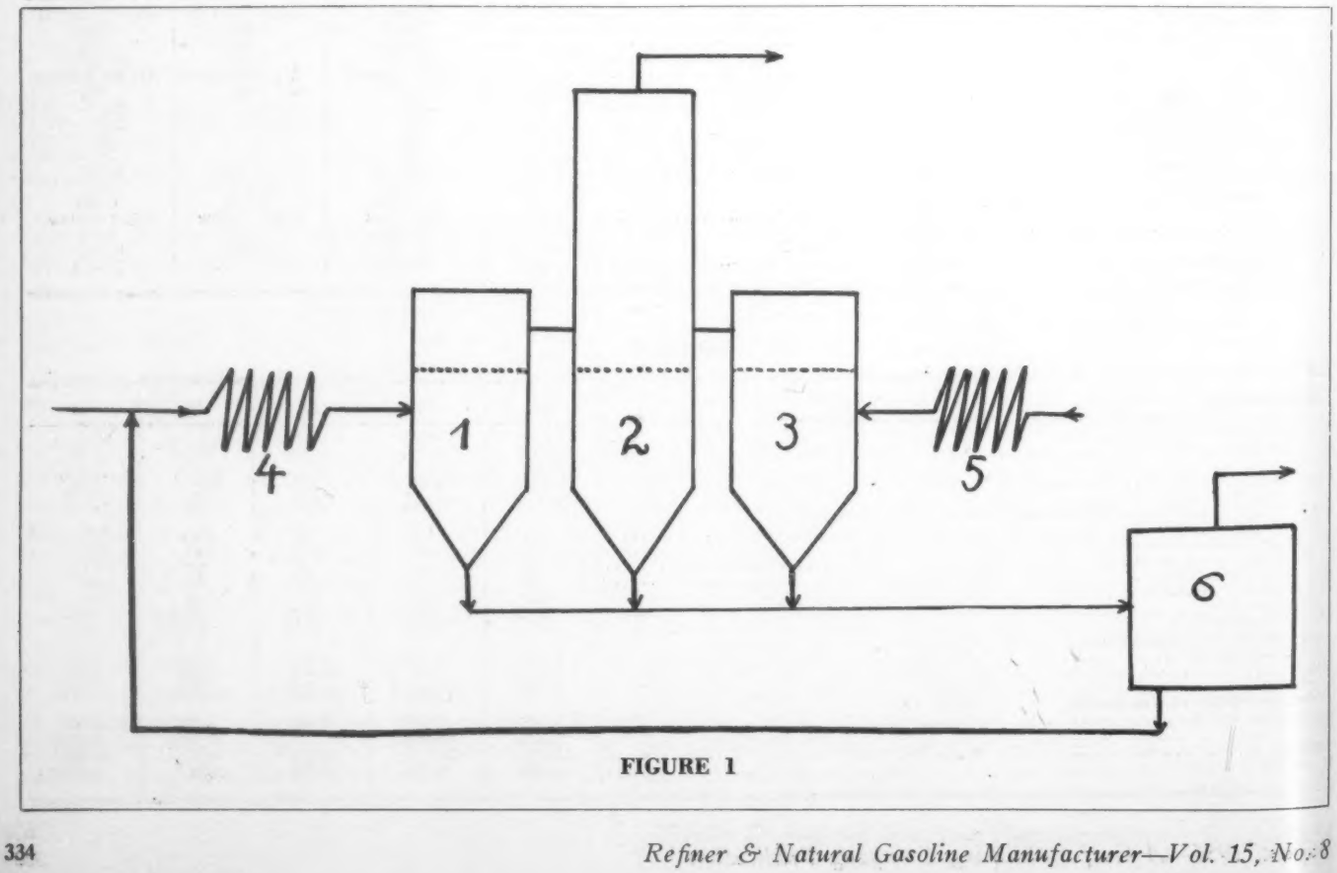


FIGURE 1

parcels of methane and the other split hydrocarbons will take place securing, in consequence, an increase in the gasoline yield. As catalyst a mixture of manganeze, molybdenum and tungsten sulfides has been used in this process. Methane has been heated to the temperature of 720°C. before entering the reaction chamber, and the charging stock to 475-485C°., before being submitted to the hydrogenation process in the reaction chamber. For both methane and the charging stock a pressure of about 200 Atm. has been employed.

A system embodying the principles mentioned above has been designed by the author. A somewhat simplified flow diagram of this process is shown in Figure 1.

The crude charge is pumped through exchangers (not shown in the figure) and delivered to the tube still, 4, being thus preheated to a temperature of 475-485°C. The charge flows from the tube still, 4, into the reaction chamber, 1, where a partial rupture of molecules takes place. At the same time methane is compressed and charged as compressed gas to the tube still, 5, being preheated to a temperature of about 720°C. The preheated methane flows then into the reaction chamber 3, where the rupture into new parcels and hydrogen takes place. Both the split molecules of the crude and those of methane pass into reaction chamber 2, where the polymerization and hydrogenation process occurs. The process is accelerated by means of the catalyst, mentioned above, which is placed on special decks inside of each reaction chamber. The gasoline vapors and gas produced flow upward through the top of the reaction chamber, being then delivered into a fractionation tower (not shown in the figure) where pressure is reduced to atmospheric. The final fuel oil residuum from the base of the reaction chambers 1, 2, 3 passes through the crude oil exchangers to the fractionation tower 6, where a fractionation takes place and the recycle stock is conducted to the tube still 4, to pass again through the furnace with the preheated fresh charging stock.

This process produces a high yield of gasoline which is characterized by a high octane rating, high volatility, having low sulfur content; the average being less than 0.001 percent. Aromatic and monoolefins are predominant in this product. In addition to these characteristics, the construction of this system is very simple, and the process is economic in operation.

Determination of Lead in Doctor Solution

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THE determination of lead in doctor solution often is helpful in the control of sweetening sour distillates in everyday refinery practice. Several methods have been proposed for analyzing doctor solution for lead content, most of which are time consuming. Kolthoff and Furman[1] show several methods for the determination of lead without special reference to doctor solution. One of these is performed by adding an excess of potassium chromate to the neutral lead solution in the presence of aluminum chloride, filtering off the lead chromate precipitate, redissolving the latter in dilute hydrochloric acid, and titrating the chromic acid with standard sodium thiosulfate in the presence of potassium iodide and starch. A modification of this as proposed by these authors, is the addition of a known excess of standard potassium dichromate in a volumetric flask and titrating an aliquot portion of the clear liquid with standard thiosulfate. These methods are satisfactory on freshly prepared doctor solution in the laboratory, but cannot be used on "regenerated" plant doctor due to the action of foreign reducing substances on the dichromate.

Lilly[2] describes a method whereby the lead is precipitated as sulfide, filtered, and redissolved in dilute nitric acid. The solution is neutralized with ammonium hydroxide, and the lead is precipitated this time as lead chromate. This precipitate is dis-

solved in dilute HCl and in excess of N/10 ferrous ammonium sulfate is added together with a small amount of phosphoric acid. The excess ferrous solution is titrated with standard potassium dichromate in the presence of sodium diphenylamine sulfonate as an indicator.

The method used in this laboratory is not new in principle, but is rapid and accurate for control purposes. Certain minor items of technic aid considerably in making it possible to make a lead determination completely in less than 10 minutes. The method involves the well known principle[1] of precipitating all the lead in solution with standard ammonium molybdate solution and testing for the first indication of a slight excess of molybdate with tannic acid as an outside indicator.

PREPARATION OF STANDARD MOLYBDATE SOLUTION

Weigh out about 20 grams of reagent quality $(NH_4)_6\ Mo_7\ O_{24} + 4H_2O$ and add to approximately 500 cc. of distilled water. The salt does not dissolve completely at once and the solution should be allowed to stand a day or two and filtered. The lead equivalent of the filtered stock solution is then determined by weighing out accurately about 1 gram of reagent quality lead chloride, dissolving in about 20 cc. of a saturated solution of ammonium acetate and 5 cc. of 50 percent acetic acid, and titrating with the molybdate solution using tannic acid as an outside indicator. The tannic acid solution should be about 0.5 percent tannic acid and should be freshly prepared.

Calculate the volume of the stock solution required to make one liter of a solution, 1 cc. of which is equivalent to 0.025 gram of litharge, (PbO) as follows:

$$X = 31.15\ V/W$$

where X is the number of cubic centimeters of the stock solution to be diluted to one liter, and V is the volume (cc) of the stock solution equivalent to W grams of $PbCl_2$. One cc. of this final solution is equal to one gram of PbO per liter when 25 cc. of doctor solution is used as a sample in the following analysis.

PROCEDURE

Measure with a pipette 25 cc. of doctor solution (unfiltered through paper) into a 250 cc. beaker. Add 50 cc. to 75 cc. of water and neutralize the caustic soda with 50 percent acetic acid as evidenced by a redissolving of the precipitate first formed. A large excess of acetic acid should be avoided for best results. Heat the solution to boiling and titrate while hot with standard molybdate solution until a drop or two shows a distinct yellow color with a drop of approximately 0.5 percent tannic acid solution on a porcelain plate. The volume of molybdate is directly the weight of litharge per liter in the doctor solution.

The data and results shown in Table 1 indicate the accuracy of the determinations. A sample of partially regenerated plant doctor solution was carefully analyzed for lead content, and to four different portions of this was added accurately weighed quantities of commercial litharge. The resulting plumbite solutions were also analyzed by the above method. Thus the results shown in the table involved the experimental error of two analyses on each sample. It is believed that the accuracy of the determinations is sufficient for plant operations and also for many research problems.

NOTES

1. The sample of doctor solution to be analyzed should not be filtered through paper no matter how turbid it may be, because presumable reactions with the filter paper very seriously affect the titrations.

2. At the beginning of the titration the precipitate of lead molybdate is very finely divided, but near the end point it becomes more curdy, and has a tendency to settle much more rapidly than at first. Thus the approach of the end point can be observed inside the solution.

3. If the beaker is placed under the burette in such a way that the reagent enters the solution down the wall of the beaker next the observer, it can be readily seen when the precipitation is nearly complete as the intensity of the white precipitate diminishes and near the end point the precipitation cannot be seen at all. This "wrinkle" is particularly helpful when a sample of doctor containing a considerable amount of "blackstrap" is titrated, and practically eliminates the disadvantage of the outside indicator.

4. With plant doctor solution, a slight yellow coloration will be noticed on the spot plate due to the original color of the neutralized doctor solution itself. The yellow color of the end point is very distinct with the molybdate solution recommended above which is relatively strong, (1.121 N/5.).

5. A burette with a two-way stopcock set up permanently with the bottle containing the molybdate, so that the reagent can be drawn into the burette and returned to the bottle, will simplify the operations.

6. A tank of reclaimed doctor to which fresh litharge has been added should not be tested until it is certain that the sample contains no litharge *in suspension,* because the suspended litharge will dissolve in the acetic acid-sodium acetate mixture obtained in the analysis, thereby showing the lead as plumbite to be high.

ACKNOWLEDGMENT

The author wishes to gratefully acknowledge the helpful suggestions of Mr. Norman Newton, Chief Chemist of the Wichita Falls, Texas, refinery of the Continental Oil Company.

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[1] Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, publishers (1929).

[2] Lilly, "Refiner and Natural Gasoline Manufacturer," 14, 473, October, 1935.

TABLE I

Plant Doctor g. PbO per Liter (By Analysis)	PbO Added g. per Liter	Total PbO g. per Liter (Calc.)	Total PbO g. per Liter (By Analysis)
8.8	5.76	14.56	14.4
8.8	2.15	10.95	11.0
8.8	4.87	13.67	13.55
8.8	4.10	12.90	12.75

Oiliness

Its Meaning and Value In Motor Oils Practice and Theory

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PART II

THE field of the use of oil is the engineering field. Consequently the use of oil is backed by a vast practical engineering experience, assisted by research in which, naturally, engineering methods predominate. It is for this reason that in Part I. we started with a practical example to demonstrate the applicability and fruitfulness of modern physical chemistry to lubrication problems. We are aware of the fact that we can "just lubricate" without any physico-chemistry. However, the more efficiently we wish to utilize our natural oil resources and modern engineering development as regards our mechanical equipment, the more it becomes necessary to get an insight into the finer differentiations of the matters we are dealing with. As the engineer of today uses physico-chemistry, metallography and x-ray methods for developing his constructions from a mechanical point of view, the oil man must look to physico-chemistry for help in developing his products to the standards imposed by the potential efficiency of modern engineering design.

Thus, our considerations shall be based upon the physico-chemistry of the processes and of the substances involved. In the present paper these properties are only considered as far as the lubricating process *in itself* is concerned. Questions of oil stability, for instance, are not discussed here. Our starting points are the general physical properties of the oils and the molecular forces which are ultimately responsible for their effective use and how lubricating properties can be investigated and predicted from this point of view.

1. *Chemistry of oils.*—Understanding "oil" very generally, from a lubrication point of view, we have to deal with three types of hydrocarbon compounds: chain compounds, cyclic compounds and the intermediate type represented by their combination. All are entirely "saturated" in so far as they are built up by tetravalent carbon atoms, aromatics, containing the benzene nucleus being practically absent in lubricating oils and, thus, scarcely an "oiliness" ingredient. Among such ingredients, as a rule rather additions, we have compounds which all have in common the C=O group and often contain the C=C group.

2. *Electric structure of matter.*—The predominance of electrical or optical methods in the study of the properties of matter is based upon the connection between electricity and matter, i.e. our conception of the electric structure of the atoms as positive nuclei with planetary systems of negative electrons. What we are dealing with here are these planetary systems which combine to form the molecules. Thus, the study of the action of an electric field on the electrons is comparable to a chemical test, with the essential difference that this action is passing with the field, leaving the molecules unaltered. Such an external electric field is, furthermore, not different in principle from the electric fields of force which the molecules built up themselves in consequence of their electric structure. Thus, we are led to the conclusion that the molecular forces which determine their physico-chemical properties are electric fields of force.

3. *Polarizability and electric moment.*—The very interaction between the external field and the molecular field of force, as represented by the discrete electric charges of the electrons means attraction or repulsion: the planetary or electron systems are subject to distortion or deformation. This electric distortion is termed "polarizability" ($\overline{\alpha}$). The result of the electric distortion is a separation of the positive and negative centers of electric charge of the molecule, resulting in an *induced* electric moment (μ_i), comparable to the well known induction effect which a conductor undergoes in an electric field. As a result, the molecule is no more electrically neutral, it becomes a *dipole*. The magnitudes of $\overline{\alpha}$ and μ_i depend on the molecular structure and are, in general, different in different directions of the molecule as will be presently demonstrated. The polarizability is measured by determining the dielectric constant (ε) and represented by the Clausius-Mosotti formula

$$\frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{M}{d}=\frac{4\pi}{3}\cdot N_A\cdot\overline{\alpha}$$

where N_A is Avogadro's number, M the molecular weight and d the density. In general and in the gaseous state, for which this formula holds rigidly, $\varepsilon=n^2$,

where n is the refractive index, and we obtain the Lorentz-Lorenz formula

$$\frac{n^2-1}{n^2+2}\cdot\frac{M}{d}=\frac{4\pi}{3}\cdot N_A\cdot\bar{\alpha}=P_E$$

the well known molar refraction where we may often take with sufficient approximation for n the value of n_D for sodium light. Thus, the molar refraction is identical with the "electronic" polarization P_E and we must emphasize in this connection that P_E does not contain the generally small contribution P_A (atomic polarization) of a slight shift of the heavy nuclei of the molecules and that a slight difference between the values of both expressions with *liquids* is normally due to the fact that $n \neq n_D$ and to the incorrect application of the formulae to the *liquid* state, not, however, to any "slight" permanent moment of the molecules.

Such *permanent* moments, or dipoles, are associated with any bond between different atoms, but being vectors, may compensate each other partly or altogether according to the symmetry of the molecule. Methane CH_4 has a zero moment, $CHCl_3$ $\mu = 1.05 \times 10^{-18}$ electrost units, whereas CCl_4 has the moment zero. As the example of CH_4 and measurements show, the small moment of the C-H bond is compensated by the moment of the CH_3 group, confirming the tetrahedral arrangement and yielding the resulting moment zero for all paraffins.

In an electric field the *permanent* moments tend to orient themselves in the direction of the field with their *definite* positions in the molecules. Molecules with such an uncompensated moment are termed polar molecules. This orientation is opposed by the heat motion of the molecules. In contrast, a non-polar molecule acquires no angular moment in a homogeneous field, its *induced* moment μ_i lying, in a first approximation, always in the direction of the field.

The formula of Debye[1] which takes account of the permanent moment

$$\frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{M}{d}=\frac{4\pi}{3}\cdot N_A\left(\bar{\alpha}+\frac{\mu^2}{3KT}\right)$$

where T is the abs. temperature, u the (permanent) moment, and k the Boltzmann constant, shows that the dipole moment adds a definite contribution to the dielectric constant ε which decreases with increasing temperature. Neglecting atomic polarization, we may write $P = P_E + P_O$ where P is the molar polarization, P_E the electronic contribution (molar refraction) and P_O the orientation contribution, all for the gaseous state. On the principle of vector addition the moments of the individual groups or bonds, such as C—H, C=C, C=O, OH, may be calculated in this way by measuring the ε of suitable compounds. As an approximate rule we may add that an $\varepsilon > 3$ points to a polar contribution, involving a larger deviation from Maxwell's relation $\varepsilon = n^2$, whereas small deviations, notably in the liquid state, are no criterion.

4. *Dielectric properties and molecular structure.*—The measurement of dipole moments and their principle of addition yield an efficient and widely used means of determining molecular structures, supplemented by the methods of light scattering and electric double refraction (Kerr-effect) with non-polar molecules. As pointed out above, the induced moment μ_i, (which both types of molecules have in common), lies in a first approximation in the direction of the field. This is rigidly so in strictly symmetrical molecules. Actually, most molecules are unsymmetrical, for instance the n-paraffins. With such molecules we may distinguish between three main polarizabilities α_1, α_2, α_3. This is a very essential point in their physico-chemical behavior, $\bar{\alpha}$ and the dielectric constant or the molar refraction measuring the average value

$$\bar{\alpha}=\frac{\alpha_1+\alpha_2+\alpha_3}{3}.$$

The rule of Silberstein[2] is a convenient means of predicting the directions of α_1, α_2, and α_3 with reference to molecular structure. Let us assume the simple case of a di-atomic molecule (Figure 1), where $-\xi$ is the electric field influencing (or "polarizing") the atoms as

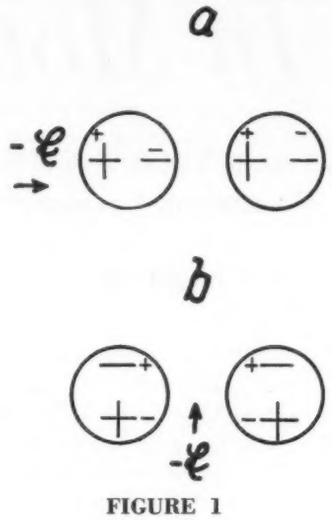

FIGURE 1

indicated in *a* and inducing the moments indicated by the large + and — signs. Obviously the negative charge of the left atom will induce another, smaller, positive charge in the right atom, superimposing itself on the charge initially induced by the field and vice versa, *increasing* the latter. Turning to *b* we see that the reverse is the case when we turn the direction of the field by 90°, thus, getting a *smaller* polarizability. Thus, in a straight chain paraffin the direction of greatest polarizability coincides with the long axis of the zig-zag chain.

5. *Valency angles and rigidity of molecules.*—Whether such a high polarizability becomes effective, i.e. whether the molecule actually assumes its straight form, depends on its general structure, on the density and on temperature. First, the chain members, the CH_2— groups, may freely rotate around the C—C bond in the practically rigid angle of this bond, which, as all valency angles, can be only *little* distorted by intramolecular action, for instance of neighboring substituents. Second, if the molecule is far enough apart from the influence of other molecules and the temperature low enough, the intramolecular forces will tend to coil the molecule up. An example of the action of intramolecular forces is the well known fact that isoparaffins with vicinal side chains show a marked increase in density compared with the normal ones. In the highly condensed states of oils, both in bulk and in boundary adsorption layers it is legitimate to assume that the stretched forms are by far predominant.

6. *Molecular forces.*—The last paragraph demonstrates in principle the essential difference between the gaseous and the liquid states, the similarity of which is generally overrated because both of them appear equally amorphous to most methods of measurement. The ex-

tension from thermodynamics to molecular physics takes account of the van der Waals forces effective in the liquid by considering electric models of the molecules and consequently electric attractive and repulsive forces. In the cases of molecules with a high degree of electric asymmetry, dipoles, it is obvious that a negative electron approaching the + pole will be attracted and, near the — pole, repulsed (Figure 2*a*. In view of the fact that the repulsive forces decrease with a much

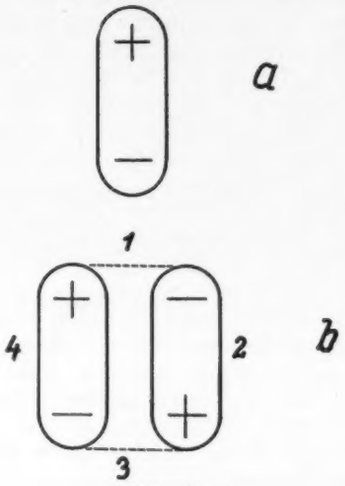

FIGURE 2

higher power of the distance*, than the attractive, this conception would do at first sight for such asymmetric molecules as shown in Figure 2*a* and yield a resulting attractive force. The more symmetric the molecule, however, the greater the difficulties which at first led to the assumption of a quadrupolar (Figure 2*b*, oktupolar, etc., distribution of charge, where, as is readily seen, there are more positions (1, 2, 3, 4) where forces on any outward charge are compensated. Meanwhile it has been demonstrated that molecules like the rare gases have too high a degree of symmetry to lend themselves to this representation, although, as a matter of fact, they are liquefied only at very low temperatures. Roughly, on the foregoing assumption, such substances should really be "permanent" gases. Moreover, as we saw in discussing molar polarization, any orienting effect of polar charge distributions should vanish at sufficiently high temperatures. We saw, however, also that $\overline{\alpha}$ is practically independent of temperature. Its influence and the actual *dynamical* character of all molecular arrangements—in contrast to our "frozen" drawings—was taken into account by *Debye*[1] and developed on the basis of quantum mechanics by *London*[3] with regard to the forces between highly symmetric charge systems as they occur in the substances with which we are concerned—the hydrocarbons.

Thus, while there are two main causes determining molecular interaction, i.e., the forces which disturb the free rotation of neighboring molecules: the electric moment and the polarizability, there are chiefly three types of forces according to our present conceptions, substantiated by experiment:

(1.) The dipole- alignment- or orientation-effect (Keesom[4]), an interaction between any dipoles present which tend to orient themselves—or to align each other, which is quivalent—so that the potential energy becomes a minimum. Figure 2*b* represents such a position and our considerations above demonstrate that it corresponds to a higher "saturated" state, i.e., one of lower potential energy than two separate dipoles. The effect always results in attraction. It is proportional to μ^2/r^3 where r is the distance of the dipoles and it decreases with increasing temperature as heat motion increases.

(2.) The induction-effect (Debye[5]), introducing into the theory of van der Waals, forces the mobility of the charges within the molecules, i.e., polarizability, in general and legitimately assuming such a mobility also with dipole charges. The mechanism is so important for *all* considerations on molecular interaction that it shall be explained on a particularly illustrative case.

Let us disregard in Figure 1*a* the external field ξ and let the circles represent two polar molecules, the large signs representing the permanent moments. Each moment is the origin of an electric field which influences the other. First, we notice the superimposed polarization (due to the interaction between the moment of the inducing molecule and $\overline{\alpha}$ of the other), indicated by the small signs. Second, the *mobile* original dipole charges will, as the molecules approach each other, like the poles of a magnet, follow the mutual attraction. Thus, the distances of the + and — charges in the individual moments will *increase*. Both effects tend to increase the original moments. The reverse happens when equal signs of different molecules face each other. Now, while the orientation effect of rigid dipoles or quadrupoles (see 1) vanishes at high temperatures, these polarizability effects are independent of temperature and always result, statistically, in attraction. The effect is proportional to $\alpha\mu^2/r^6$ and its origin is electric fields of molecules, produced by dipoles or by a statistical asymmetry of their charges. The effect is very small when this asymmetry is small. However, if we could take extremely quick snapshots of the electronic motion, we should detect quickly changing highly unsymmetrical constellations even in the most symmetric molecules, resulting in:

(3) The "dispersion" effect (London)[3,6], proportional to $\overline{\alpha}^2 . V_i/r^6$, where V_i is the potential of ionisation (removal of one electron) of the molecule and it should be noted that α is in this case squared. The contribution of this effect to the molecular forces is often of the order of the dipole effect and entirely dominates when the dipole moments are small.

B—APPLICATIONS: THE LIQUID STATE, VISCOSITY PHENOMENA

7. *The liquid state.*—In the liquid state all of the three effects become effective to a various degree which depends essentially on the magnitude of μ, α, on the temperature and the distance between the molecules. In this distance we should perhaps include an individual structural property of the molecules, best termed "accessibility" and equivalent to the stereochemical notion of degree of sterical hindrance and which obviously must depend upon molecular flexibility. The rigidity of valence angles comes into play here. Thus, if we compare the triangular molecule H_2O with CH_3OH (methanol), it is obvious that the OH moment is shielded (less accessible) from the CH_3 side, while in ether $(C_2H_5)_2O$, this screening effect goes still farther. On the other hand, we cannot expect anything like a considerable dipole effect between hydrocarbon molecules with their small C-H moments; whereas we should expect a difference in magnitude of the effects depending

*i.e. within the normal molecular distances there prevails attraction as statistical calculations show. On trying to compress the liquid, a rapidly increasing resistance is observed, arising from the repulsive forces. These are not considered here, where we are dealing with the comparatively compressible liquid state in a fairly high temperature range.

upon α in different directions with such oblong molecules or flat molecules like benzene. As a result of the influence of *distance* we should expect that *small* polar molecules become, in general, effective as units, while with larger or rod-shaped molecules, or with molecules where strong group moments are compensated (CCl_4), *individual* group = partial moments become effective. These are the general rules which should serve as a guide in approaching particular problems experimentally.

It has long been known that in liquids, the molecules of which contain OH, COOH, or NO_2 groups, groups which we now call polar groups, molecules are likely to be "associated." We see at once that measurements of the electric moments of such substances in solutions of non-polar liquids (hexane, benzene, preferably *not* such with large "partial" moments, like CCl_4) should give an indication as to the degree of association, on which, in general, the magnitude of the moments will depend according to the way the molecules align each other. The fact that dipole effects are so strongly localized that there are in several cases well known and very stable dimolecular (formic, acetic acid, even in the vapor state) and perhaps even definite polymolecular states,[7] explains why this effect was longer known and attributed to some "abnormal" behavior of such substances. In most cases this behavior is also manifest in such properties as heat of vaporization, critical point, surface tension, etc.

The development of experimental methods, e.g., the x-ray method, made possible a more general demonstration of such association effects. Thus, for the n-paraffins, alcohols and fatty acids *Stewart* and his co-workers[8] demonstrated the existence of states of order in the liquid state which are in agreement with our knowledge of the molecular forces. We are justified in admitting the "cybotactic" state as quite a normal one and as an expression of the fact that there must be states of minimum potential energy of longer life in liquids than states of higher potential energy. In many cases we can even approximately compute which states these are. Thus, with normal paraffins and with any "long" molecules of this kind such bundles of molecules will be on the average more stable, where the greatest number of atoms will be most close together, i.e., where the molecules lie like matches in a match-box. Their spacing in the cases investigated by Stewart and his co-workers is 4.6 A.—units, much the same as in the crystalline state, while the CH_2 groups in the zig-zag chains are 1.54 A. apart. Furthermore, since the direction of maximum polarizability coincides with the length of the rod (see Figure 1), we must conclude that, when adsorbed on a surface, as in a lubricating boundary layer, the most stable position must be the position where the bundles stand head on the surface. For such an orientation there is still other evidence.[9]

The same reasoning applies to the flow-orientation with decrease of viscosity of lubricating oils, advanced as a hypothesis by the author a few years ago.[10,11] It is measured by means of a machine designed by Prof. Prandtl[12] and is another method of demonstrating the cybotactic state which yields in the same experiment the actual drop of viscosity by this orientation and comparative estimates of the length of the oil molecules and of their coefficient of static friction. There are only very small forces necessary to produce flow orientation, as experiment shows, and, the smaller the forces producing it, the longer must be the molecules which form the bundles. This orientation results, as a matter of course, in optical anisotropy which may be measured as double refraction on transparent oils.[13]

8. *Viscosity phenomena.*—As far as well defined compounds were investigated—in the paraffin series—branched isomers show a lower viscosity than the normal hydrocarbons[14] and less saturated a higher viscosity than the saturated,[15] as would follow from the foregoing considerations. The general increase of viscosity within a homologous series or within an equivalent series of lubricating oils was discussed in an earlier paper.[16] There is not enough experimental material available on the lines proposed here and the oils are too complex to allow definite conclusions to be drawn. However, it is well known that paraffinic oils of high viscosity (about SAE 60) have much higher molecular weights than the corresponding naphthenic oils and a rather different temperature coefficient of viscosity. In view of the fact that with all hydrocarbon oils the forces involved are practically exclusively the dispersion forces, this behavior would suggest an essentially different molecular structure, as suggested in the author's paper cited above. Molecules, in which cyclic structures are prevailing, of the type of cyclohexane, which, in contrast to benzene rings, are not *plane,* might well have a higher density, owing to their lower hydrogen content *and* to some close *intra*molecular packing, but, notwithstanding be less accessible to the fields of force of neighboring molecules. This would mean a very great anisotropy of the polarizability with a weak lateral field of force, *quickly* decreasing with decreasing density, i.e., with increasing temperature. As should be expected on this tentative hypothesis, two typical naphthenic oils with viscosities at 20°C. of 13 and 7.6 Poises showed practically the same decrease in viscosity by flow orientation, 8 percent, whereas a typical paraffinic oil (11 P. at 20°C.) showed a decrease of only 7.4 percent. The molecular weights of these oils were 426 and 382 for the naphthenic and 825 for the paraffinic, the average lengths of the molecular complexes involved about the same.

As the author pointed out elsewhere there is no essential difference between the viscosity curves of mineral and fatty oils, which is quite plausible from the standpoint of molecular forces. The "polar" oils form clusters or smaller complexes by dipole association, their long chains screening any resting free dipole forces so that essentially, as far as viscosity is concerned, the same forces will come into play as with the mineral oils. The suggestions for further research in this field are obvious.

(*To be concluded.*)

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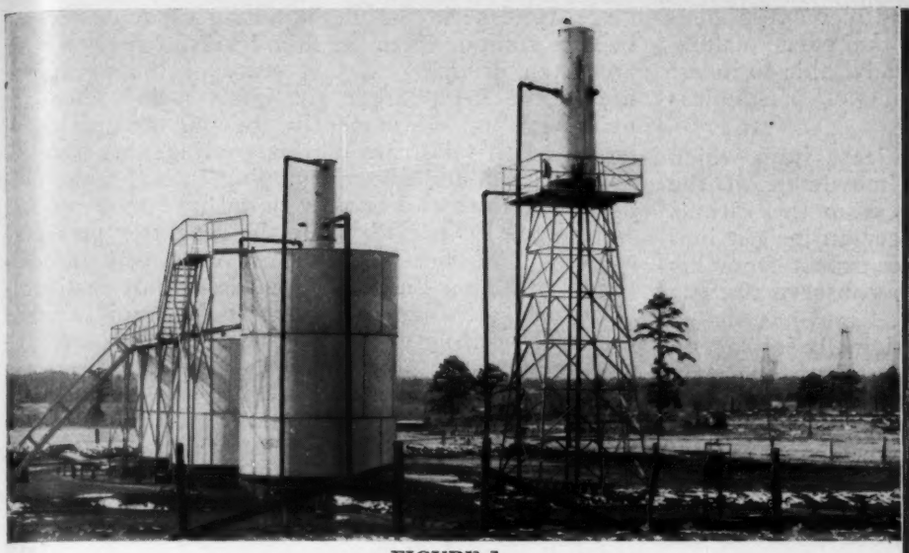
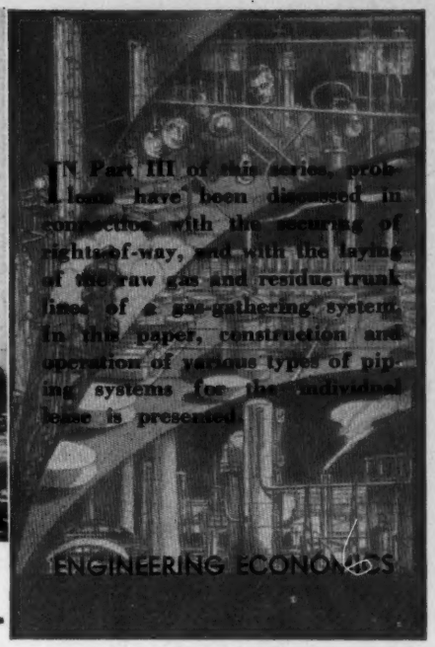


FIGURE 1
Oil-gas separator, elevated in order to reduce operating back-pressure.


IN Part III of this series, problems have been discussed in connection with the securing of rights-of-way, and with the laying of the raw gas and residue trunk lines of a gas-gathering system. In this paper, construction and operation of various types of piping systems for the individual lease is presented.
ENGINEERING ECONOMICS

Construction and Operation of Natural Gasoline Plants

PART IV

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GAS GATHERING SYSTEMS—THE LEASE LINES

THE gas contract between the oil producer and the natural gasoline manufacturer generally specifies that the latter return the residue gas to the edge of the oil producing lease and that the raw gas be transported from the wells to the gasoline plant. The trunk lines, therefore, take care of the delivery of the residue gas, as the oil producer is supposed to pipe the dry gas over the lease. The gasoline manufacturer is under obligation to lay raw gas lines directly to the wells or oil-gas separators, which means that a small gathering system must be installed on each lease. Although these lease gathering lines are much smaller than trunk lines, the same degree of accuracy should be carried out in determining their size. The chain of lines carrying the gas from the well to the plant is no more efficient than its weakest link or bottle-neck constriction. In other words, there is no need to add trunk lines if the lease lines cause abnormal pressure drops between the wells and the point where the gas leaves the lease to enter the trunk line.

GAS MEASUREMENT

The measurement of gas is of paramount importance since the payment is based on the record provided by the orifice meter charts. Developments in the measurement of gas have been very rapid. During the first 20 years in the life of the natural gasoline industry all gas measurement was done through either positive or proportional gas meters. These positive meters gave a fair degree of accuracy for small gas volumes, but when it came to the measurement of large volumes, the meters of this type proved to be not only too bulky, but also expensive both from standpoint of investment and from the cost of maintenance and repair. In the past 15 years these positive meters practically all have been replaced by various types of orifice meters.

Each lease, no matter how few wells may be upon it, must have an orifice meter. This meter usually is equipped with a 24-hour chart on which a written record is kept of the differential pressure across the orifice plate, as well as the static pressure on the downstream side of the plate. This differential may be taken at a distance of 2½ diameters upstream and 8 diameters of the pipe downstream, or it may be recorded by means of connections in the orifice flange itself. These meters give accurate measurements provided they are taken care of by well trained meter men. The maintenance cost on orifice meters does not run high except in new fields where sudden flows of gas may cause the loss of some mercury into the gas lines, and in certain sour-gas

areas where hydrogen sulphide and mercaptan compounds may cause corrosion of the parts making up the meter. On "sour-gas" it is advisable to invest in meters equipped with either monel or stainless steel parts.

The meters are located on the lease from which the gas is being purchased. A knowledge of the accurate measurement of the gas from the various leases helps to give the oil producer an insight into the future reserves which he can expect from his lease. It is also to his interest to conserve the gas energy stored up in the reservoir. Katz[2] has shown how the quantity of oil and gas originally in place in the reservoir can be calculated by statistical data taken from the field from time to time. These data include the amount of produced oil and gas and the bottom hole pressure in the reservoir at various dates during the life of the field. Solubility-shrinkage data, as determined by Lindsly[3], are also needed for such reservoir calculations. The measurement of return residue gas for the flowing of gas lift wells is of equal importance since the difference between the raw gas production and the input gas represents the formation gas. Whenever the input gas registers more than the raw output gas, it is time for the producer to change his method of operation since such a result shows that gas is being forced back into the reservoir. This phenomenon often occurs in fields being produced by gas lift, especially when the bottom hole pressures have been falling rapidly.

DETERMINATION OF LINE SIZES

In a number of fields where the wells have been allowed to produce large volumes under comparatively low pressures, it has been found economical to lay temporary gas gathering lines of large size on the surface of the ground. This proved to be the case in fields such as the Burbank district in Northern Oklahoma where there is little farming, and the leases were developed rapidly with no proration restrictions. In fields of this kind which flow wide open, the decline in gas volumes is rapid so that within a few years the temporary surface lines may be taken up and be replaced by smaller permanent lines buried well below the surface of the ground. With the present tendency toward the proration of new producing fields, it is questionable whether temporary lines laid on the surface would be advisable. The advent of gas lift has had a tendency to prolong the flowing life of the field. There is also a trend toward flowing the wells against a greater back pressure than was the practice 10 years ago. For these reasons the first lines to be installed on a lease may well be permanent buried lines.

As a field approaches the period when the wells can neither flow naturally nor be produced against a back pressure with gas lift, the producer resorts to the practice of lowering the back pressure on the wells down to atmospheric pressure in order to gain the greatest amount of expansive power developed by the release of dissolved gas from the crude oil. This lowering of pressure can sometimes be accomplished by raising the separator so that the oil can gravitate to a storage tank. Figure 1 shows a photograph of one of these separators which has been so elevated. This period in the life of the field is a trying one for the gasoline producer since the rapid drop in pressures on the gas separators means a large decrease in the gas handling capacities of the booster station. Since the fluid levels in the reservoir are often dropping at this stage of the producing life of the field, larger gas input ratios often are necessary and consequently the gas production is increased to take care of this contingency. To prevent large volumes from popping into the air, new gathering lines and booster units have to be added. If this gas lift period, while the separator pressures are low, is of short duration, an investment in additional gathering lines and boosters is not justifiable since the gas volumes are apt to fall rapidly when the wells go from gas lift to the pumping stage. The gasoline manufacturer therefore tries to convince the oil producer that it is to his advantage to maintain a certain amount of back pressure on the separators to increase the gas deliveries into the gasoline plant. While such an argument does carry some weight, the oil producer realizes that every additional pound in pressure drop that he can effect upon the separator will mean a large amount of increase in the available work resulting from the expansion of the gas which is flowing the well. This can be illustrated clearly by referring to a pressure vs. volume curve Figure No. 2 on a sample of original bottom hole crude taken from Wilcox sand in the Oklahoma City field[3]. On this same figure is plotted the isothermal expansion curve for a perfect gas. Since the available work energy is equal to the integral of the pressure times the change in volume or $\int Pdv$ the area under the pressure volume curve between any two pressure limits represents the foot pounds of energy released per pounds of original bottom hole fluid. This area can best be found by graphical integration through the use of a planimeter, or by estimating the number of squares present. Figure No. 3 shows the percentage of expansive energy released as a function of pressure. It is interesting to observe that only 40 percent of the energy has been released when the pressure has fallen to as low as 250 pounds per square inch. In actual operation, however, the dissolved gases are not released as differentially as they were in the laboratory, therefore the pressure volume curve would probably fall somewhat above the differential-flash curve in field practice. Graphical integration shows that approximately three horsepower is developed in the differential expansion of a barrel of the original crude oil from the Wilcox sand in the Oklahoma City field.

CHANGING THE LINES TO CASINGHEAD CONNECTIONS

When the pressure on the sand reservoir has decreased to the point where gas lift devices such as intermitters, plunger lifts, etc., can no longer be used economically, the wells are then put on the beam. It is not advisable however to tie into the casingheads of such pumping wells for some time, since these wells often head up and flow when the well is not pumping. Therefore the casinghead connections should be piped through the oil-gas separator until there is practically no danger of the well flowing naturally.

There are several types of lease gathering systems which may be laid out on a 160-acre tract. These systems are shown in Figures 4, 5, and 6. Figure 4 shows the piping arrangement for a lease on which 4 separators have been so located as to take care of the 16 wells during the natural flow and gas lift

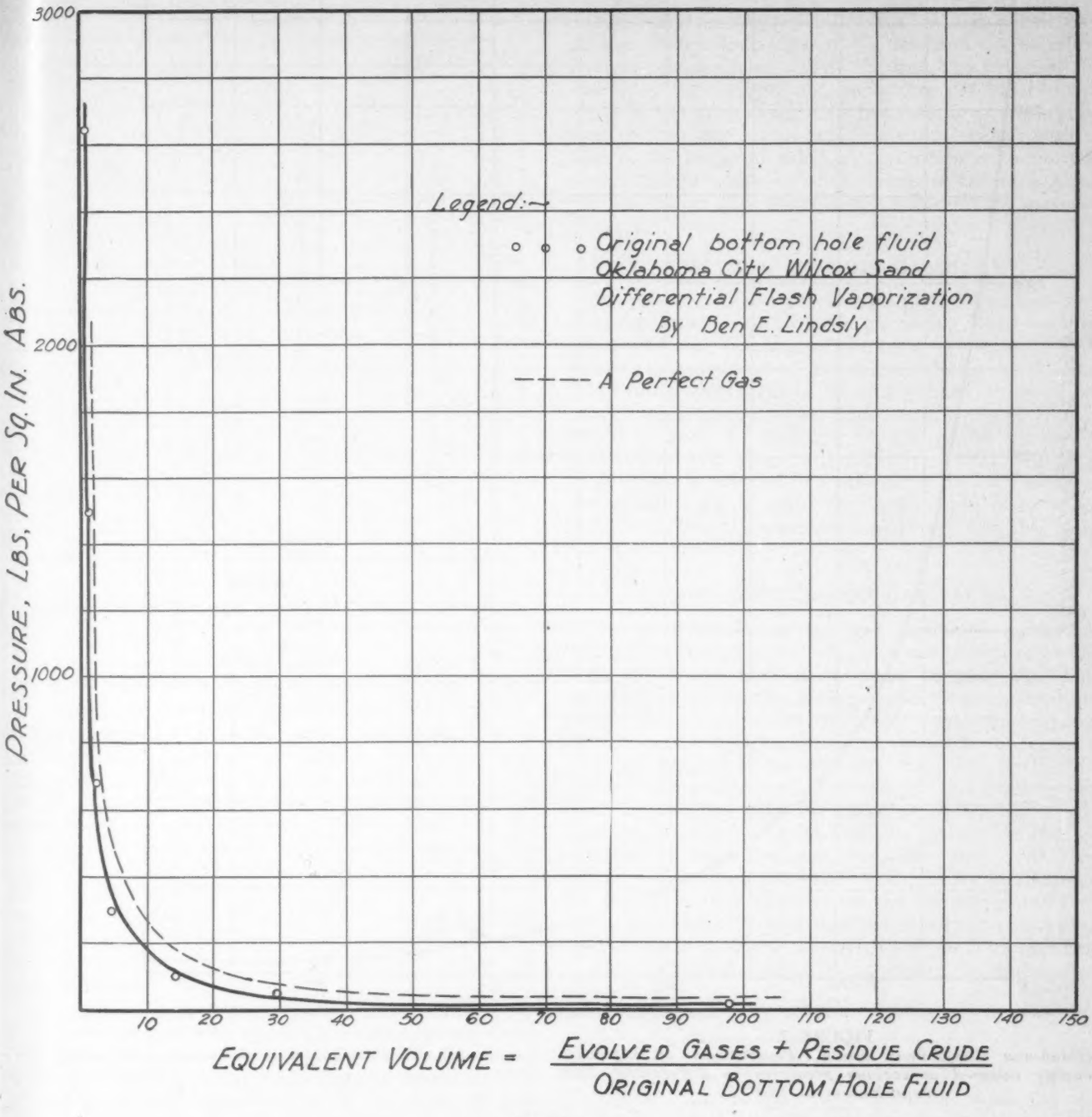
3000
2000
1000
PRESSURE, LBS, PER SQ. IN. ABS.
Legend:—
Original bottom hole fluid
Oklahoma City Wilcox Sand
Differential Flash Vaporization
By Ben E. Lindsly
A Perfect Gas
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
EQUIVALENT VOLUME = EVOLVED GASES + RESIDUE CRUDE / ORIGINAL BOTTOM HOLE FLUID

FIGURE 2
Pressure vs. Volume Curves at 130° F.

periods. In this case it is assumed that the oil lines to the 4 separators will be left as permanent lease lines. Figure 5 shows a layout of lines for a lease where the separators have been placed near each well or between pairs of wells. From this layout it is evident that less pipe is required as shown in Figure 4 since none of the gas has to travel in a direction away from the meter setting such as is the case with wells 2, 4, 13 and 15 in Figure 4.

The third type of lease gathering system is shown in Figure 6. This type is known as the loop system. Although more piping is required than in lease systems shown in Figures 4 and 5, it has a certain degree of flexibility which the other systems do not have. For example, if repair has to be done on a part of the loop, certain block gates can be closed and the gas from the remaining wells can be handled around the other side of the loop during the time the repair work is being carried on.

PROBLEMS CONNECTED WITH VACUUM OPERATION

It has been common practice in the Mid-Continent fields during the past 20 years to pull a vacuum on the oil producing leases after the wells have been put to pumping. This is increased from year to year until it finally reaches within ½-inch to 1-inch of absolute vacuum. In such fields it is necessary to maintain a vacuum which is substantially equal on each and every well. If this equal distribution of vacuum is not obtained, the leases on which less vacuum is pulled, often suffer heavy gas drainage to other offsetting leases. If the lines on the lease are fairly large in size, one back pressure regulator

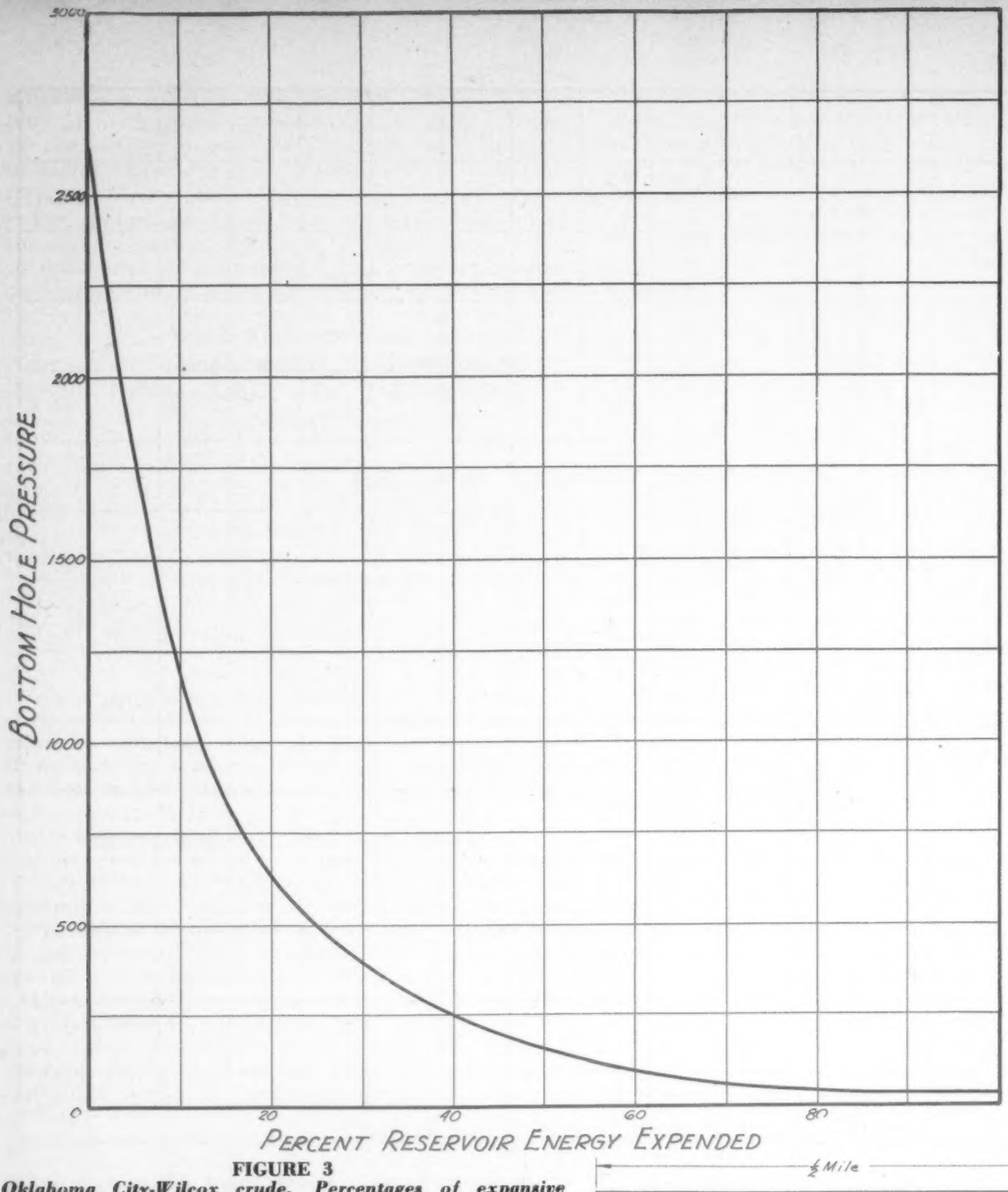

FIGURE 3

Oklahoma City-Wilcox crude. Percentages of expansive energy released at various pressures in differential flash vaporization at 130° F.

located at the meter setting will assure a uniform vacuum over the lease. If a finer adjustment is desired, it is necessary to set a back pressure regulator near each well. On these leases, all of the casingheads are equipped with ¼-inch connections so that regularly scheduled vacuum tests can be made with a mercury manometer to determine the distribution of vacuum between the many wells and leases.

AIR INFILTRATION

Perhaps the most serious problem which arises from the maintenance of vacuum on oil-producing leases is that of the infiltration of air due to leaks in the pipe lines and through the open casings of wells which are being cleaned out. The admixture of air tends to lower the plant efficiency in that it requires a higher pressure in a compression plant to obtain the same degree of extraction, and in the case of an oil absorption plant, the oil circulation must be increased in order to offset the higher percentage of air. Air causes the partial pressure of the gasoline

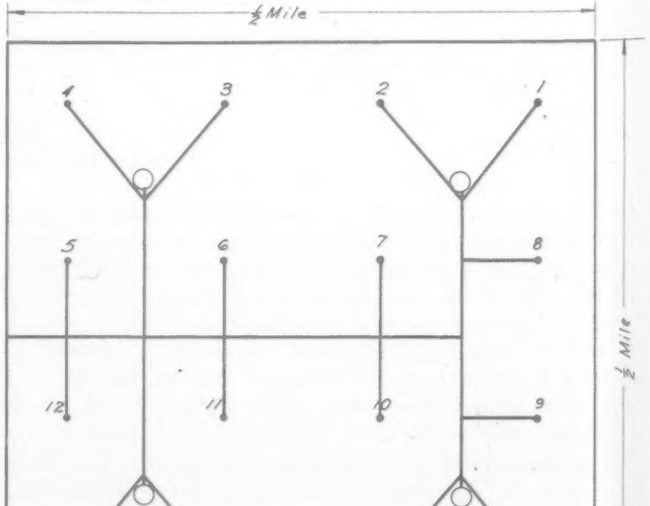

FIGURE 4

Branch system for lease with four oil-gas separators.

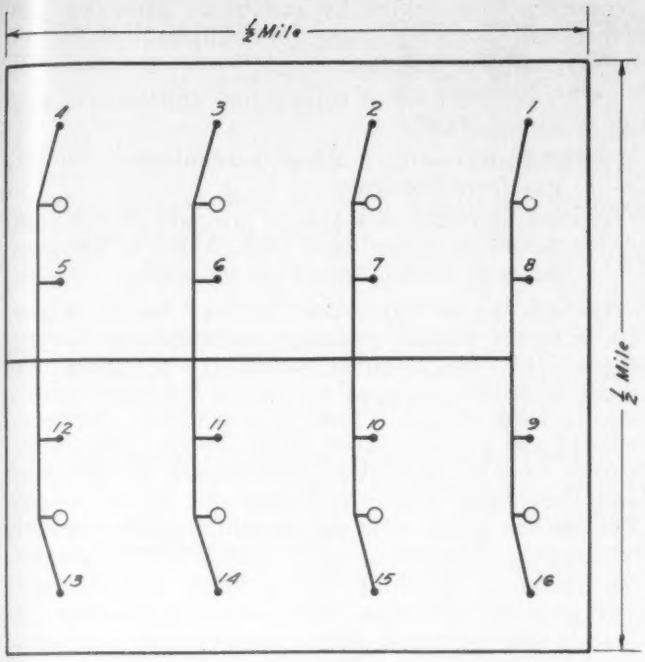

FIGURE 5
Branch system for lease with eight oil-gas separators.

constituents to be lowered, thereby reducing their driving force or absorption tendency throughout the length of the absorber.

The danger of explosion from the accumulation of high percentages of air is not likely to occur unless the air percentage reaches 80 percent or more. If the incoming raw gas has a gasoline content of about 1 gallon per 1000 cubic feet of gas and the air amounts to 20 percent, the residue gas may be expected to have around 20.6 percent air. However, if the gas contains 20 gallons of gasoline per 1000 cubic feet, 20 percent of air in the incoming gas will result in about 50 percent of air in the residue gas. In Figure 7, the above two examples are shown in diagrammatic form.

Air leakage causes an increase in the rate of internal corrosion of pipe lines. This effect is especially noticeable in areas where gases contain hydrogen sulphide resulting in the deposition of iron sulphide in pipe lines, and in the oxidation of hydrogen sulphide to form water and free sulphur.

METHODS OF DETECTING AND COMBATTING AIR INFILTRATION

The gasoline plant which operates on high vacuum has to make frequent tests on the air content of the incoming gas. Whenever this air content increases, the task of locating the air leaks is sometimes difficult. A test usually is made on each trunk line coming into the plant by obtaining samples with small hand-operated vacuum pumps. If the air leakage is coming from some gas line on a lease, it usually can be detected by a sudden increase in the volumes passing through the orifice meter. After the line which is causing the air leakage has been located, it often is difficult to find the exact place where the leak is occurring. If the line is buried, the cost of removing the dirt covering the line is generally prohibitive. The quickest and surest method of locating the leak is to shut off the line and allow a small amount of pressure to build up on the particular sector. If the leak cannot be detected by smelling the gas which blows out of the line, the firing of the line may be carried out as a last resort. Caution must be taken in doing this because large accumulations of gas may occur which are not readily noticeable to the sense of smell. A torch tied onto the end of a long wire may serve the purpose for such firing operations, in case there is no inflammable material along the line.

DISPOSAL OF DRIP GASOLINE

In older fields the percentage of the gasoline production which forms in the gathering lines may be an appreciable fraction of the total production. This is especially true on all booster discharge lines operating under pressures of several pounds or more per square inch gauge. The lines must be kept free of liquid in order to maintain their capacity up to the maximum. The drips are locked so that the theft of gasoline is reduced to a minimum. In cold weather the gasoline plant sends trucks to these drips regularly to collect the gasoline and bring it to the plant for redistillation.

THE FREEZING OF GAS LINES

Practically all natural gas contains a certain amount of water vapor which is apt to freeze in the lines in winter and cause them to plug up. This problem is especially serious in high-pressure lines where the combinations of water vapor and hydrocarbons cause hydrates to form. These hydrates have a much higher freezing point than ice itself[1]. To combat the problem of "freeze-ups" the troublesome parts of the line may be kept hot by means of gas heaters. Another method is to inject alcohol or calcium chloride solution into the line. The line which is frozen on the inside can usually be detected by the formation of frost on the outside surface of the pipe. These "freeze-ups" generally occur where constrictions or bends happen to be in the pipelines.

The gathering system is no better than the men

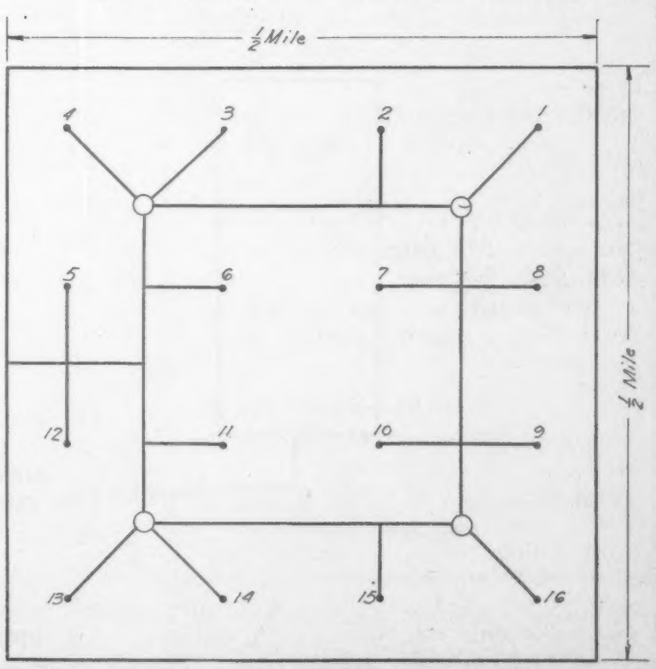

FIGURE 6
Loop system for lease with four oil-gas separators.

who are responsible for its operation. Although the gasoline manufacturer buys gas he is really out to sell service to the oil producer and the line walker forms an important link in rendering this service. Since the field lines are not as accessible as the plant, many superintendents are prone to overlook the operation of the gas gathering system. Since the bringing of gas into a plant is such an important part of the scheme of operations, it is becoming a practice in large gasoline producing districts to turn over the supervision of the gas-gathering system to the head meter man or chief gas tester.

The line walker has various duties to perform outside of such regular routine jobs as keeping the lines free of liquid and reporting serious gas leaks. Above all he must keep in touch with what is going on in the field and show on the back of the gas charts the causes for unusual changes in the gas volumes coming from each lease. If the residue gas line, going to a lease, should freeze up, the producer may allow pressure to build up on some of the casingheads in order to supply fuel for his lease. The line walker must be on guard to see that these emergency fuel lines are shut off after the gas system is thawed out so that no residue gas will recycle back into the gasoline plant. To make a long story short, the line walker is a very important cog in the operation of any gasoline plant for without him the plant could not depend upon a steady supply of raw material from which it can manufacture its products.

If the natural gasoline manufacturer expects to obtain future gas contracts without difficulty, he must necessarily give good service to all of the oil producers from whom he purchases gas. The producer will have no cause for complaint if he can be assured of

(1) a steady flow of return fuel and recycle residue gas
(2) the processing of a high percentage of the raw gas from the lease
(3) maintenance of a steady pressure on the separators or casingheads comparable to the pressures prevailing on adjoining leases.

In turn the producer may be expected to cooperate with the natural gasoline manufacturer. In prorated fields the producer should try to handle the wells in such a way as to supply the plant with a steady load of gas. There is a tendency, however, toward the production of all of the oil early in the month causing excessive gas volumes at that time and very little gas toward the end of the month. The producer can help the gasoline plant operators by keeping them informed of changes in oil producing methods. In old pumping fields the producers can give the gasoline plant a much steadier gas load if they can agree upon a plan to pump an equal number of wells at all times during the day and night, and in return the producers can be assured of a more nearly constant supply of return residue or fuel gas from the gasoline plant.

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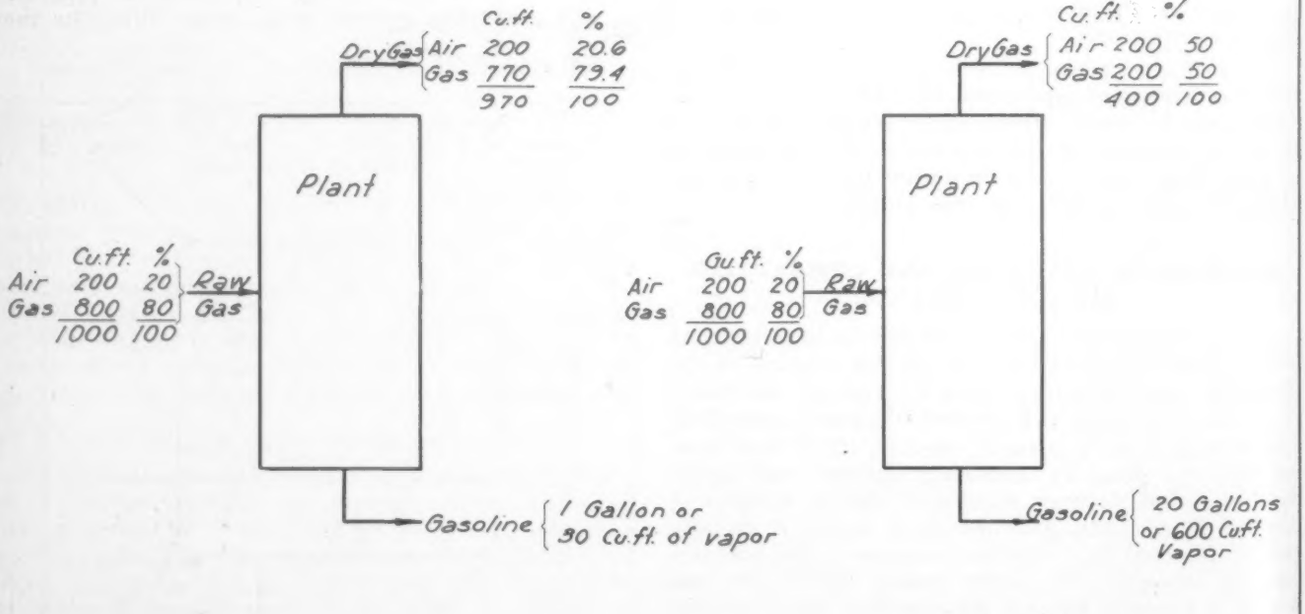

FIGURE 7
Diagrammatic sketches showing changes of air percentages in gas as result of gasoline extraction.